FINAL REPORT

Evaluating Long-Term Impacts of Soil-Mixing Source-Zone Treatment using Cryogenic Core Collection

ESTCP Project ER-201587

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14. ABSTRACT

A former source zone containing TCE DNAPL was remediated using soil mixing with zero valent iron and bentonite, a technology referred to as ZVI-Clay Soil Mixing. Four years of remediation performance data suggest that peak groundwater and soil concentrations have been reduced by >4 orders of magnitude, and groundwater TCE concentrations have approached MCLs. This project assessed the long-term impacts of ZVI-Clay Soil Mixing, in terms of rebound potential and effects on natural processes. Existing soil and groundwater data were supplemented with high-resolution data, generated using cryogenic core collection, for several parameters including chlorinated ethylenes, gaseous products, inorganic parameters, and soil properties. The evaluation suggested that contaminant concentration rebound appears unlikely within the treated source zone, due to the low contaminant mass remaining, ongoing apparent reactivity of ZVI toward TCE, and lack of heterogeneity within the mixed-soil zone. Downgradient of the treated zone, the concentration distribution suggests that long-term site management may be strongly affected by chlorinated ethylene mass in low-*k* zones. However, the presence of degradation products, including ethylene and acetylene, suggest ongoing degradation is occurring outside of the mixed-soil zone, and degradation may be occurring within low-*k* zones. Downgradient treatment may also be affected by uncertain groundwater flow patterns.

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ACRONYMS AND ABBREVIATIONS

112-TCA	1,1,2-Trichloroethane
APP	Accident Prevention Plan
C_3	Cryogenic Core Collection
*c*DCE	*cis*-1,2-dichloroethylene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFRB	Contaminant Flux Reduction Barrier
CIL	Core-In-Liner
CME	Central Mining Equipment
CSM	Conceptual Site Model
CSU	Colorado State University
DADI	De-Aired Deionized (water)
DCE	Dichloroethylene
DCM	Dichloromethane
DEI	Drilling Engineers Inc.
DIW	Deionized Water
DNA	Deoxyribonucleic Acid
DNAPL	Dense Non-Aqueous Phase Liquid
DoD	Department of Defense
EISB	Enhanced In Situ Bioremediation
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
f_{oc}	Fraction Organic Carbon
ft bgs	Feet Below Ground Surface
GC	Gas Chromatograph
GC/ECD	Gas Chromatograph /Electron Capture Detector
GC/FID	Gas Chromatograph /Flame Ionization Detector
GC/MS	Gas Chromatograph /Mass Spectrometric Detector
GSI	Groundwater Services Inc.
HASP	Health and Safety Plan
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatograph
ID	Inner Diameter
IDW	Investigation Derived Waste
ISCO	In Situ Chemical Oxidation
K	Hydraulic conductivity

LN	Liquid Nitrogen
Low-*k*	Low-permeability
MSD	Mass Spectrometric Detector
µg/L	Micrograms per liter
mg/kg	Milligrams per kilogram
mg/L	Milligrams per liter
MNA	Monitored Natural Attenuation
MTBE	Methyl Tert Butyl Ether
ND	Non Detect
ng	Nanograms
NPV	Net Present Value
NSFIH	Naval Support Facility Indian Head
OD	Outer Diameter
OHSU	Oregon Health & Science University
PAH	Polyaromatic Hydrocarbon
PCE	Perchloroethylene
PRB	Permeable Reactive Barrier
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
qPCR	Quantitative Polymerase Chain Reaction
RCRA	Resource Conservation and Recovery Act
RNA	Ribonucleic Acid
SERDP	Strategic Environmental Research and Development Program
SIM	Single Ion Mode
TCE	Trichloroethylene
*t*DCE	*trans*-1,2-Dichloroethylene
UXO	Unexploded Ordinances
VC	Vinyl Chloride
VOC	Volatile Organic Compound
ZVI	Zero Valent Iron
ZVI-Clay	Soil mixing with ZVI and bentonite (Clay)

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Colorado State University personnel provided help on many levels with the processing and analysis of the frozen cores. Undergraduate research assistants, including Christina Ankrom, Tyler Cloud, and Anna Hoyt, played an important role in preparation and processing of the samples. Junior Garza and Bart Rust machined the cryogenic coring tools used for this project.

Rick Rogers from Drilling Engineers Inc. has been instrumental behind development of the cryogenic coring tools and procedures used in this project. The field crew from Drilling Engineers Inc., Dustin Coy and Andy Lozano, were masterful in operating cryogenic coring equipment and efficiently solving problems encountered in the field.

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EXECUTIVE SUMMARY

Objectives of the Demonstration

This project is designed to assess the long-term performance of a remediation technology applied to a dense non-aqueous phase liquid (DNAPL) source zone. The remediation technology evaluated, herein referred to as ZVI-Clay Soil Mixing, involves deep-soil mixing with zero valent iron (ZVI) and bentonite (Clay). In November 2012, the ZVI-Clay Soil Mixing technology was used to remediate a trichloroethylene (TCE) DNAPL source zone at Site 17, Naval Support Facility Indian Head, Maryland (Site 17). Four years of remediation performance data indicate that TCE concentrations in soil and groundwater within the treated-soil zone had been reduced by up to four and five orders of magnitude, respectively. Groundwater concentrations in portions of the former-DNAPL source-zone have approached MCLs within four years of soil-mixing completion.

Following the positive treatment results of the ZVI-Clay Soil mixing remedy, the overarching goal of this project was to assess post-remediation potential for TCE concentrations to rebound, as well as effects of remediation on natural fate-and-transport processes. To achieve this goal, high-resolution data representing both high-permeability (high-*k*) and low-permeability (low-*k*) soil strata was imperative. To satisfy this data need, cryogenic core collection (C_3) was implemented.

The project included four specific performance objectives:

1. Supplementation of existing remediation performance data with high-resolution data for key parameters.
2. Assessment of biogeochemical conditions in the treated source-zone.
3. Generation of data to improve understanding of downgradient and low-*k* zone processes.
4. Evaluation of core recovery and production rate achieved by cryogenic coring.

Technology Description

The Site 17 project involved two technologies: the ZVI-Clay soil mixing remediation technology (completed in 2012) and the C_3 characterization technology (implemented in 2016). Although the ZVI-Clay Soil Mixing remedy was completed prior to implementation of the project described herein, description of both technologies is presented.

ZVI-Clay Soil Mixing. The ZVI-Clay Soil Mixing remediation technology involves admixing ZVI and bentonite into chlorinated-solvent source zones using large-diameter augers. The ZVI-Clay Soil Mixing technology creates a relatively homogeneous distribution of contaminants and reactants, thus overcoming challenges of geologic heterogeneity and incomplete reagent delivery that limit treatment performance of many remediation technologies.

ZVI-Clay Soil Mixing at Site 17 (conducted prior to this ESTCP-funded project) was completed over two weeks in November 2012. The targeted mixing zone at Site 17 included 1300 yd^3 of soil from a depth interval of 2 to 18 feet below ground surface (ft bgs). The soils were admixed with target amounts of 1 to 3% ZVI (excess ZVI was added to potential DNAPL areas) and 0.5% bentonite.

Post-remediation performance assessment at Site 17 included soil and groundwater data collected on a quarterly to annual basis. Performance assessment was primarily based on groundwater data, which was collected from two locations within the mixed-soil zone and six locations outside the mixed soil zone. Soil samples were collected, using direct push techniques, from locations within three of the mixed-soil columns to evaluate concentration changes over time.

C_3 characterization. This project supplemented the existing performance data via a detailed assessment of site conditions four years after remediation was implemented. C_3 techniques were used to characterize the contaminants and biogeochemical conditions in the treated body and adjacent plume. The C_3 technology involves freezing soil cores *in situ* and then conducting high-resolution analysis on the frozen cores. The C_3 technique provided a natural fit for the characterization needs of this project.

Cryogenic coring was conducted in June 2016, four years after remediation. Sampling was conducted at six locations, including two within the treated zone and four downgradient (plume) locations. Frozen soil cores were collected following procedures developed under previous work funded by Strategic Environmental Research and Development Program (SERDP; projects ER-1559 and ER-1740). Upon collection, the frozen cores were placed in a cooler on dry ice, and subsequently shipped to a laboratory via overnight delivery.

Processing and analysis was conducted by Colorado State University (CSU). While frozen, cores were cut into subsamples and processed for high-resolution analysis of key parameters including chlorinated ethylenes (TCE, *c*DCE, and VC), gaseous degradation products (methane, ethane, ethylene, and acetylene), inorganic parameters (chloride, sulfate, and iron), and soil properties (bulk density and clay content). Additional testing, including ZVI content, reactivity, and biological analysis, was conducted on select samples.

Demonstration Results

Existing performance assessment data suggested that the remediation has substantially reduced chlorinated solvent concentrations within the former DNAPL source zone. Within the source area, maximum pre-mixing concentrations for TCE, *c*DCE, and VC were 1500, 220 and 80 mg/L, respectively. These concentrations provide strong evidence that TCE DNAPL was present in portions the source zone prior to remediation. Four years after remediation, the peak TCE concentration was 0.015 mg/L, a reduction by five orders of magnitude. Intermediate degradation products, *c*DCE and VC, have subsequently declined to 0.18 and 0.25 mg/L, respectively. Outside of the treated-soil zone, limited impacts of the remediation are apparent in groundwater monitoring data. The lateral extent of the plume has not changed significantly, and minor increases in TCE degradation-product (*c*DCE and VC, respectively) concentrations were noted in one downgradient monitoring well. Overall, the monitoring results outside the treated zone suggest that downgradient impacts may be affected by hydraulic changes imposed by soil mixing.

The C_3 characterization at Site 17, which was conducted under this project, supplements the existing remediation performance data with high-resolution geochemical, biological, and reactivity data. Within the treated source zone, the C_3 geochemical data suggest that conditions are generally homogeneous. The highest measured TCE concentration was 0.3 mg/kg, which is four orders of magnitude lower than the highest pre-mixing TCE concentration (510 mg/kg).

Gaseous product concentrations are relatively limited within the treated zone; acetylene was not detected in any sample, and ethylene was non-detect in 29 of 35 samples from within the treated interval. These observations are consistent with the low levels of chlorinated ethylenes remaining in the treated soil zone. ZVI content and reactivity testing confirmed that reactive ZVI remains present and is capable of reacting with chlorinated ethylenes. These results suggest that little contaminant mass remains stored in the source zone, and future releases (i.e., rebound) of chlorinated ethylenes from the treated-soil zone are unlikely.

The downgradient concentration distribution suggests that long-term site management may be affected by chlorinated ethylene mass residing in low-*k* zones. Of two transects evaluated in this project, high-resolution data from one (referred to as transect DG2) suggest TCE concentrations up to 75 mg/kg occur within the underlying low-*k* aquitard. The presence of ethylene and acetylene provides evidence that biological or abiotic reductive dechlorination of TCE, *c*DCE, and VC occurs within low-*k* zones in transect DG2. Data from the other transect (transect DG1) suggest little-to-no detectable chlorinated ethylenes occur in the underlying clay. In the low-*k* clay zone associated with transect DG1, gaseous products consist primarily of methane and ethane; declining concentrations versus depth suggest that diffusion may be responsible for the distribution of these compounds in the low-*k* zone. The absence of ethylene and acetylene in the clay aquitard is consistent with the lack of local chlorinated ethylenes in transect DG1.

In conclusion, source zone remediation appears to have been highly effective at Site 17, and current conditions appear amenable to ongoing assimilation of TCE and related products. Contaminant concentration rebound appears unlikely within the treated source zone, due to the low contaminant mass remaining, continued apparent reactivity of ZVI toward TCE, and lack of heterogeneity within the treated soil zone. Downgradient of the treated zone, the presence of chlorinated ethylenes in low-*k* zones, and assimilation processes occurring within these low-*k* zones, are likely to govern plume longevity. The C_3 data may support future modeling efforts to evaluate the back-diffusion potential related to contaminant mass storage in low-*k* zones associated with the dilute plume, outside of the treated zone at Site 17.

Implementation Issues

Although the ZVI-Clay Soil Mixing technology was completed four years prior to the ESTCP-funded portion of this project, implementation issues described in the Soil Mixing Completion Report (prepared by CH2M HILL) are presented herein. The primary issue associated with soil mixing involved buried wood, which was encountered over much of the area under Site 17; the buried wood was excavated prior to soil mixing. No other substantial implementation issues were documented in the Soil Mixing Completion Report.

The primary issue with cryogenic coring involved limited core recovery in the mixed-soil zone. The limited recovery was likely related to softness of the bentonite-mixed soils, which restricted soil entry into the core barrel. This issue was not attributed to the cryogenic coring process, i.e., the same issue would likely have occurred using conventional (i.e., unmodified) hollow-stem auger equipment. For future implementation of cryogenic coring in soft soils (possibly including sediments), additional modifications to the sampling apparatus may be required to improve recovery.

Other cryogenic coring issues, which resulted in minor delays, included (a) buried wood affecting sample recovery, (b) coring equipment freezing downhole, and (c) freezing or binding of the core sample in barrel. No major changes in implementation are recommended to address these issues, as the issues were readily addressed in the field and solutions did not result in lengthy delays.

1.0 INTRODUCTION

Few chlorinated solvent source zones, especially those that have been impacted by dense non-aqueous phase liquids (DNAPLs), have been remediated to low concentrations such as maximum contaminant levels (MCLs). Remediation performance of most technologies is constrained by subsurface heterogeneity, which often limits concentration reductions to about 1 to 2 orders of magnitude (Stroo et al. 2012). A method to overcome the limitations of subsurface heterogeneity involves soil mixing for reagent delivery (Olson and Sale 2015). Soil mixing with zero valent iron (ZVI) and bentonite (Clay), herein referred to as ZVI-Clay Soil Mixing, is an emerging technology for remediation of chlorinated solvent source zones (Olson et al. 2012). This report describes post-remediation performance assessment at Site 17, Naval Support Facility Indian Head (NSFIH), Maryland (Site 17), where a former source zone containing trichloroethylene (TCE) DNAPL was remediated via ZVI-Clay Soil Mixing in November 2012. Since treatment at Site 17, groundwater concentrations in monitoring wells within the treated zone have declined by approximately 4 to 6 orders of magnitude, to concentrations at or near MCLs.

Following the source-zone remediation at Site 17, additional questions remain:

- What is the fate of the relatively small amount of chlorinated solvents that persist in the source zone?
- Is the ZVI still reactive toward chlorinated solvents?
- What are the long-term impacts of the source-zone soil mixing on downgradient groundwater and soil?
- To what extent will contaminants residing in low-permeability (low-*k*) zones affect longevity?

This project addressed these questions via collection of high-resolution, multi-parameter data from Site 17 using Cryogenic Core Collection (C_3) techniques. The C_3 techniques involve freezing soil cores before their removal from the subsurface, thus enhancing core recovery and preserving *in situ* properties during core removal and analysis. The results of the sampling conducted herein are evaluated with existing Site 17 remediation performance data to provide enhanced understanding of soil-mixing remediation impacts and ongoing processes.

The project team included Trihydro Corporation (Trihydro); Colorado State University (CSU); Dr. Rick Johnson of Oregon Health & Science University (OHSU), who participated in this project as an independent consultant; and Drilling Engineers Inc. (DEI). Points of contact are presented in Appendix A.

1.1 BACKGROUND

This project addresses environmental problems associated with the remediation of source zones of chlorinated solvent releases at Department of Defense (DoD) sites. Two specific areas are addressed: (1) performance assessment of chlorinated solvent source-zone remediation using ZVI-Clay Soil Mixing, and (2) efficient generation and use of high-resolution multi-parameter data for performance-assessment. This subsection presents a brief description of both; detailed descriptions are provided in Section 2.0.

ZVI-Clay Soil Mixing.

The ZVI-Clay Soil Mixing technology was developed as a means to overcome heterogeneity (Olson 2014). Implementation of the technology utilizes traditional soil mixing equipment for reagent delivery. Following soil-mixing remediation, reagent-contaminant contact issues are eliminated via the combination of (a) uniform delivery of ZVI; (b) homogenization of soils, and subsequent elimination of low-*k* zones; and (c) re-distribution of contaminant mass, including DNAPL. Furthermore, through the addition of bentonite and blending of soil strata of contrasting permeability, the hydraulic conductivity of the mixed-soil region is reduced, typically by one or more orders of magnitude. The combination of ZVI-mediated degradation and reduction in hydraulic conductivity can reduce contaminant flux by many orders of magnitude (Olson and Sale 2015).

As of May 2014, the ZVI-Clay Soil Mixing technology had been applied at five DoD sites (Olson 2014): Arnold Air Force Base, TN (Palaia 2007); Indian Head, MD (CH2M HILL 2013); Lake City, MO (Killenbeck et al. 2008); Warrenton, VA (Ruffing et al. 2008); and two applications at Camp Lejuene, NC (Bozzini et al. 2006 and Olson et al. 2012). Results to date have indicated that the ZVI-Clay technology is effective in providing source removal and/or isolation.

Remediation Performance Assessment Using Cryogenic Core Collection.

The C_3 sampling technology involves freezing soil cores *in situ* by circulating liquid nitrogen (LN) through a cavity in the core-collection tool. The frozen core is then removed to the surface and placed in a cooler on dry ice (-80°C) for shipment. The sample is shipped to a laboratory for processing and analysis. Processing techniques have been developed for the frozen cores, which provide high-resolution data for a variety of biogeochemical parameters.

Advantages of collecting soil cores cryogenically, as compared to conventional soil coring methodologies, include improved soil recovery, little-to-no drainage of pore fluids, and preservation of sensitive parameters such as volatile contaminants, gas-phase degradation products (methane, ethane, and ethylene), microbial content, and redox-sensitive species (e.g., iron and sulfur compounds) (Sale et al. 2016 and Kiaalhosseini et al. 2016). Furthermore, processing of the cores can be conducted in the laboratory, where handling and extraction is more controlled than in the field, thus reducing the potential for losses of volatile constituents and other biogeochemical transformations.

1.2 OBJECTIVE OF THE DEMONSTRATION

The primary objectives of the demonstration project included assessing the contaminant distribution and biogeochemical conditions of the ZVI-Clay Soil Mixing technology, four years after implementation, at locations within the (remediated) former source zone and downgradient of the treated-soil zone. Within the treated-soil zone, this objective included evaluating the permanence of the remediation, in terms of the potential for future concentration rebounding to occur. Downgradient of the treated-soil zone, the project objective included evaluating geochemical conditions (e.g., contaminant distribution and natural degradation potential) in areas where groundwater advection, back diffusion, and natural assimilation processes are expected to govern timeframe required for cleanup. This assessment was done using C_3 site characterization techniques (as previously advanced under ER-1740) to generate high-resolution multi-parameter data.

1.3 REGULATORY DRIVERS

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as well as the Resource Conservation and Recovery Act (RCRA) are both federal statutes that require cleanup of soil and groundwater contamination, and which provide the governing regulatory framework at numerous DoD facilities. These programs may be led by the U.S. Environmental Protection Agency (EPA) or may be state-led, depending on the jurisdiction. Both RCRA and CERCLA require control and/or treatment of release source areas, as well as treatment of plumes emanating from source areas. DoD Instruction 4715.06, dated May 4, 2015, requires that "*environmental programs in the DoD achieve, maintain, and monitor compliance with all applicable environmental requirements*," such as may be required under RCRA or CERCLA.

Site-specific cleanup plans often involve source removal/isolation as a means to ultimately gain improvements in groundwater plumes emanating from the source. However, impacts of source removal/isolation on plume characteristics are currently not well understood, and our ability to elucidate these effects is limited by traditional sampling methods (Sale et al. 2013). For example, by eliminating contaminant mass input into a downgradient plume, diffusion gradients can be reversed, thus triggering back-diffusion from low-*k* soil zones (Chapman and Parker 2005; Sale et al. 2008), but the back-diffusion process is difficult to monitor due to sampling technology limitations. Also, natural degradation processes (biological and abiotic) might have a much greater impact on plume longevity in the lower-concentration environment resulting from source removal. Overall, the potential long-term limitations and advantages of source-zone removal have been the focus of considerable debate (e.g., Kavanaugh et al. 2003, Stroo et al. 2012, Falta and Kueper 2014.

Within the context of these regulatory drivers, this project was designed to address the following questions:

- What are the long-term performance expectations of ZVI-Clay Soil Mixing?
- What are the groundwater quality parameters, four years after implementation?
- What processes govern groundwater quality, both within and downgradient of the mixed soil zone?

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2.0 TECHNOLOGY

This section provides an overview of the ZVI-Clay remediation technology that is the subject of the performance evaluation herein, and the C_3 characterization technology that was used in this evaluation. ZVI-Clay Soil Mixing has been used at several DoD installations over the past 10 years (as discussed in Section 1.1). The C_3 characterization technology was developed under Strategic Environmental Research and Development Program (SERDP) projects ER-1559 (Johnson et al. 2012) and ER-1740 (Sale et al. 2015). Additional details on both technologies are provided in this section.

2.1 TECHNOLOGY DESCRIPTION

2.1.1 ZVI-Clay Soil Mixing

The ZVI-Clay Soil Mixing technology has been documented in detail elsewhere (Olson et al. 2012, Fjordbøge et al. 2012a and 2012b, Olson 2014, and Olson and Sale 2015). This section presents summary information on implementation details, technology development history, and envisioned applications.

An illustration of the soil mixing process is shown in Figure 1. Implementation of the ZVI-Clay technology utilizes crane- or trackhoe-mounted soil mixing equipment (Figure 2), depending on the scale of the site. The ZVI and bentonite may be mixed in a grout plant, or dry-mixed into the soils. In most applications, the bentonite is combined with water in a portable grout plant; the ZVI is then mixed with the grout for delivery. The grout, with suspended ZVI, is then pumped into the subsurface via ports in the soil mixing tool. To accomplish mixing, the soil-mixing tool is rotated and simultaneously driven downward or upward in the subsurface, thus creating vertical mixed columns (Figure 1). The typical mixed-soil column diameter, which is determined by the size of the soil mixing tool, is 8 to 12 feet. With each mixed column, several mixing passes are typically completed to ensure adequate mixing. Mixed soil columns are overlapped to ensure that the entire target area is treated (Figure 1).

During mixing, quality control measures may be implemented to ensure specifications are met. Samples may be collected and analyzed for ZVI content using a magnetic separation method. Collecting soil samples for total contaminant concentrations may be beneficial for performance evaluation, as post-mixing concentrations are often enlightening and sometimes surprising.

After mixing is complete, soils tend to be soft and have a high water content. Mixed soils might not be able to support the weight of a vehicle or drill rig for periods of weeks to months after mixing, as the soils consolidate. The consolidation process can be accelerated by applying a surcharge (i.e., pile of soil for extra weight) to accelerate draining of excess water.

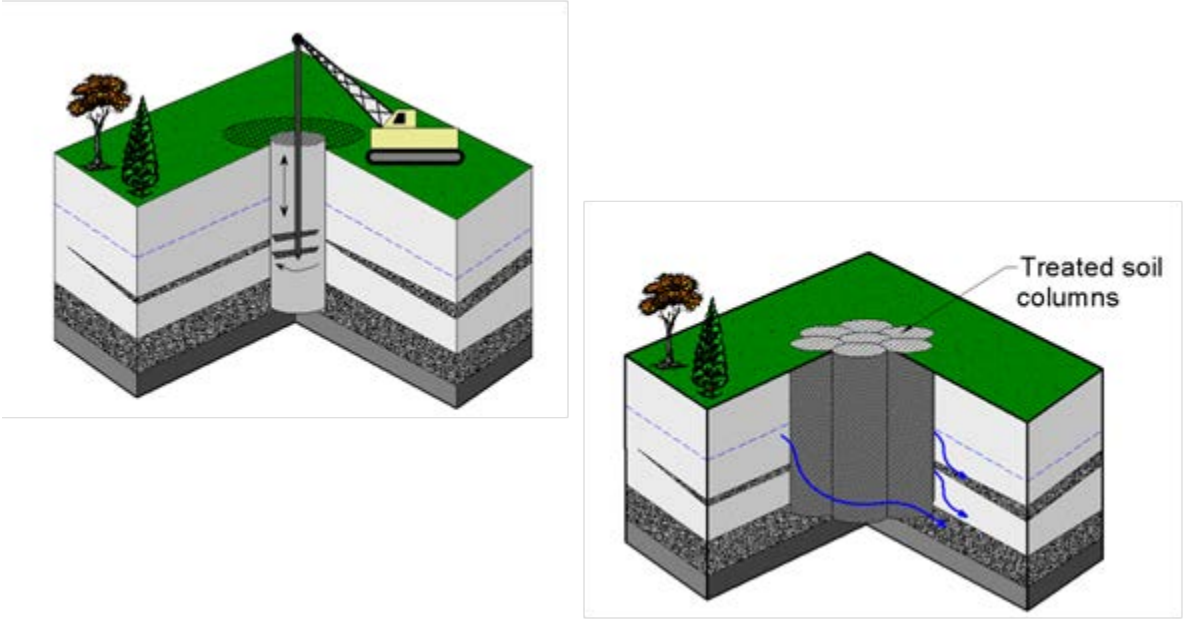

Figure 1. Soil Mixing Illustrations.

(Left) Soil mixing in progress and (right) overlapping mixed columns in a mixed soil zone (Olson 2014).

Figure 2. Photos of Soil Mixing Equipment.

(A) large scale crane-mounted soil mixing (Olson et al. 2012), (B) backhoe mounted (redoxtech.com), (C) back mounted (Langetool.com), and (D) intermediate scale backhoe mounted system, photograph taken at Waukegan, IL (owned by GeoSolutions).

Development History. Initial development of the ZVI-Clay technology grew out of work related to ZVI permeable reactive barriers (PRBs) that were developed by Dr. Robert Gillham at the University of Waterloo in the early 1990s (Gillham and O'Hannesin 1994). The idea that soil mixing could be used to deliver ZVI into high-concentration source zones was developed in the late 1990s via independent work conducted at both DuPont and the University of Waterloo. Pilot-scale testing was completed at Canadien Forces Base Borden in 2002 (Wadley and Gillham 2005) and the first full-scale field application was completed by DuPont in 2002 (Shackelford et al. 2005). In 2003, DuPont donated patents covering the ZVI-Clay technology to CSU; CSU led advancement of the technology until the patents expired in 2016. While holding the patents, CSU conducted bench-scale research and development work, delivered technical presentations at conferences, produced peer-reviewed publications, supported graduate students, and oversaw 13 full-scale field applications. The ZVI-Clay initiative has generated five peer-reviewed publications including laboratory testing methods (Castelbaum et al. 2009, Castelbaum et al. 2011, and Sample et al. 2012), modeling methods (Olson and Sale 2015), and field-scale case studies (Olson et al. 2012). Although the patent is now expired, CSU continues to conduct treatability studies for sites where the technology is being considered.

Applications. The primary application envisioned for the ZVI-Clay Soil Mixing technology includes small- to mid-scale sites where high concentrations of chlorinated solvents, potentially including DNAPLs, are present. Cost analysis has suggested that the technology is highly cost-competitive with other technologies that are capable of reaching similar performance levels, such as thermal remediation (Harkness and Konzuk 2014). The soil-mixing technology is flexible in that reagents can be selected based on the type of contaminant present and treatment goals. For example, chemical oxidants can be used in place of ZVI for treatment of polyaromatic hydrocarbons (PAHs); cement is often used as a stabilizing agent for heavy-metal impacted sites. Questions to consider when evaluating the technology include the following:

- Are the contaminants treatable?
- Is the depth and geology amenable to mixing?
- Is the site accessible?
- Are utilities/buildings a concern?
- What is the envisioned post-mixing site use?

2.1.2 Cryogenic Core Collection

The C_3 technique, which was used to collect characterization data at Site 17 as part of this project, has been documented in the final report for ER-1740 (Sale et al. 2016) and was published by Kiaalhosseini et al. (2016). Summary details are provided herein.

The C_3 technology was developed to overcome the limitations of traditional soil-coring technologies by freezing soil cores *in situ*, recovering the frozen cores at the surface, and then transporting the cores (while frozen) to a laboratory for analysis. The approach used for this project is based on a design approach that was initially developed at OHSU as part of SERDP project ER-1559 (Johnson et al. 2012), and was subsequently refined by the project team members including CSU, OHSU, and DEI, under ER-1740 (Sale et al. 2016).

The C_3 technology is based on a modified hollow-stem auger drill rig (Figure 3). The hollow-stem auger rig consists of a Central Mine Equipment (CME)-75 drill system with 4¼-in. ID auger flights and a 4-in. outer diameter (OD) Continuous Sample Tube system, manufactured by Central Mine Equipment (St. Louis, MO). The system was modified to allow circulation of LN using a coil of copper tubing (an alternative approach uses a dual-wall cylinder, in which LN is circulated in the annular space). A cylinder of ¼-in. closed-cell foam insulation was wrapped around the cooling coil (or dual-wall cooling cylinder) to direct the thermal-cooling energy provided by the LN inward to the soil core.

Figure 3. Hollow-stem Auger Drill Rig Used for C_3.

The process for collection of frozen cores is illustrated in Figure 4. Frozen cores are collected in 2½-ft sections. The general process is as follows: the auger and continuous core sampler are advanced to the desired depth, LN is circulated to freeze the core, the continuous sampler with frozen core is extracted; the process is repeated until core is collected from the entire targeted depth interval.

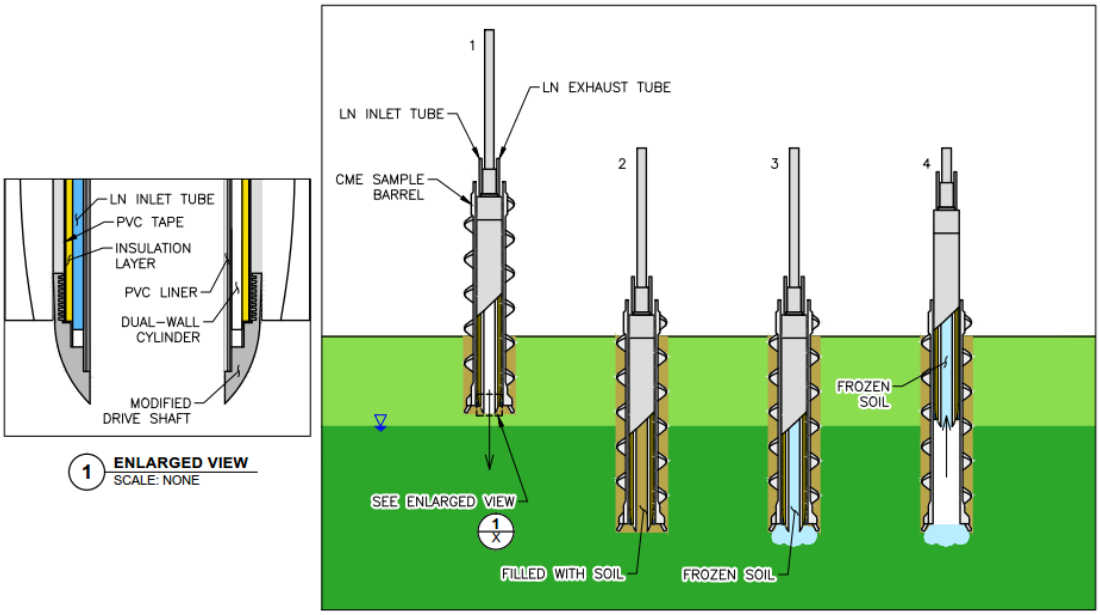

Figure 4. C_3 Schematic Illustration (after Sale et al. 2016 and Kiaalhosseini et al. 2016).

(1) the auger and continuous sample barrel are advanced, in 2.5-ft sections, filling the core liner with geologic media during auger advancement, (2) the core liner is stopped at the target depth, (3) LN is circulated, freezing the sample within the core liner, (4) the sample barrel containing the frozen soil core is removed. Steps 1-4 are repeated until the entire targeted depth interval has been sampled.

Frozen core analysis was conducted at the Center for Contaminant Hydrology laboratory at CSU, under the direction of Dr. Tom Sale. The high-throughput core analysis procedures were developed at CSU under ER-1740. Briefly, a cut-off saw was used to divide the core into subsamples, consisting of one-inch-thick discs of frozen core (Figure 5; left); subsamples can be collected at any interval, depending on project needs. The subsamples were then divided (Figure 5; right) to be analyzed for a variety of parameters. Additional details, specific to this project, are presented in Section 5.6.

Figure 5. Photos of Core Processing and Subsampling Equipment (Sale et al. 2015).

(Left) cutting of frozen core into subsections, Mitchell Olson is shown; and (right) photos of equipment used for processing: (A) cut-off saw; (B) stop blocks, used for rapid and repeatable measurement of subsample interval sizes; (C) chisel; (D) hammer; (E) Polyvinyl chloride pipe, cut to size; and (F) entire apparatus used for sub-dividing frozen soil discs.

Development Summary

A detailed description of the C_3 development history is provided by Kiaalhosseini et al. (2016). Briefly, cryogenic coring dates back to at least the 1980s. Early projects evaluated a variety of approaches to cryogenic sampling, including direct injection of LN into the formation (Yoshimi et al. 1984); circulation of liquid CO_2 through a drive-shoe chamber (Durnford et al. 1991); and a combination of the CO_2-circulating drive show with a core-barrel piston (Murphy and Herkelrath 1996). In recent development work, Johnson et al. (2012) utilized a modified drive-point system to allow for circulation of LN to freeze cores *in situ*; this work was funded under SERDP (ER-1559). Subsequently, another SERDP-funded project (ER-1740) involved development and implementation of a hollow-stem auger system for cryogenic sampling. The C_3 system developed under ER-1740, which is described in detail by Sale et al. (2016) and Kiaalhosseini et al. (2016), is the basis for the project described herein.

Applications

Since recent development under ER-1559 and ER-1740, the C_3 sampling approach has been used for chlorinated solvent and hydrocarbon sites. As of January 2017, the researchers have been involved in C_3 activities at five locations, in addition to Site 17 (the associated contaminant class of the site is indicated in parentheses):

- FE Warren Air Force Base (chlorinated solvents; described in Sale et al. 2016),
- A former refinery in Wyoming (hydrocarbons; described in Sale et al. 2016),
- A former refinery in the mid-western United States (hydrocarbons),
- A federal facility in South Carolina (chlorinated solvents),
- A private-sector industrial facility in New Jersey (chlorinated benzenes and other organic constituents).

The C_3 applications completed to date have demonstrated the feasibility of field implementation. The use of C_3 for remediation performance assessment at Site 17 represents a novel application of the technology. Implementation of C_3 for broader applications helps advance the technology beyond the demonstration scale, toward commercial viability.

2.2 TECHNOLOGY DEVELOPMENT

This project involved two technologies: ZVI-Clay Soil Mixing treatment technology and C_3 characterization technology. This project focused on assessing treatment performance of a ZVI-Clay Soil Mixing field application that was completed in 2012. Thus, no development of the ZVI-Clay Soil Mixing technology, *per se*, was conducted as part of this project. The C_3 characterization technology was employed for this project to provide the high-resolution data necessary for the performance evaluation of ZVI-Clay Soil Mixing. The cryogenic coring equipment was based on the dual-wall system as described by Sale et al. (2016) and Kiaalhosseini et al. (2016). An upgraded C_3 sampling tool was produced in early 2016 and was used for this field work. This upgraded tool was built in accordance with the dual-wall cylinder described in the references noted above.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.3.1 ZVI-Clay Soil Mixing

Advantages. The ZVI-Clay Soil Mixing technology offers the potential to treat chlorinated solvent source zones more effectively than alternative technologies. Soil mixing for reagent delivery provides simultaneous contaminant degradation and stabilization. Soil mixing overcomes contaminant/reagent contact issues and offers the potential to treat contaminant mass that initially resides in low-*k* zones. Furthermore, through the addition of bentonite and blending of soil strata comprising various particle-size distributions, the hydraulic conductivity is reduced, often by one or more orders of magnitude. The combination of contaminant degradation with reduced hydraulic conductivity may reduce contaminant flux by several orders of magnitude (Olson and Sale 2015).

Disadvantages. Three potential disadvantages should be considered when considering ZVI-Clay Soil Mixing. First, the zone targeted for treatment must be accessible for soil mixing equipment. Mixing cannot be completed under buildings (unless they are removed) and utilities or other obstructions must be considered. Second, the soils must be mixable. Sites comprising fractured rock or high content of large-diameter media (cobbles to boulders) may not be mixable. Buried obstructions may also be a cause for concern. Finally, soil mixing with ZVI and bentonite alters the load-bearing capacity of soils. After mixing is completed, an extended period (e.g., several months) may be required for settlement to stabilize. Additional geotechnical evaluation may be required to evaluate soils before building after soil mixing is complete. Here it is noted that mixing with ZVI and cement has been evaluated, as a means to enhance the strength of soils after mixing is complete; cement was found to greatly inhibit the post-treatment reaction rates, likely due to the high pH induced by cement (Olson 2014).

2.3.2 Cryogenic Core Collection

Advantages. C_3 sample collection provides several advantages over conventional soil-coring and alternative site characterization methodologies. Freezing soil cores *in situ* provides a means to generate high-resolution data that represents subsurface conditions with improved accuracy. Pore fluids, including aqueous-, non-aqueous-, and gaseous-phase organic compounds, are effectively immobilized in the frozen samples. Many geochemical properties are preserved in the frozen cores (Johnson et al. 2013), and microbial deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) is isolated from the effects of oxygen intrusion or cross-contaminant during sample handling. In addition, the frozen cores can be transported to a laboratory, where processing and analysis can be conducted more efficiently.

The data generated by C_3 can be used to build a conceptual site model (CSM) with improved accuracy and level of detail. The resulting high-resolution data can be coupled with geologic observations to identify low-*k* zones and, subsequently, to evaluate their contaminant mass storage capacity; this provides a substantial advantage over traditional groundwater monitoring-well sampling, which is inherently biased against analytes present in low-*k* soil zones. Additional advantages of C_3 are documented by Kiaalhosseini et al. (2016).

Limitations. The C_3 technology has certain limitations. These include the following:

- Certain geology types may not be amenable to hollow-stem auger soil coring, e.g., sites with high content of cobbles or other large debris;
- Sample collection takes additional time, thus cryogenic coring is more expensive than conventional coring (addressed in Section 7.0);
- Safety requirements must be adhered to for transport and handling of LN on site;
- Certain aspects of the aqueous chemistry may be impacted during freezing process – solubility of constituents may change due to decreasing temperature and/or phase change as the pore water freezes;
- Laboratory processing of samples requires specific equipment and handling procedures (e.g., cut-off saw for dividing frozen cores).

3.0 PERFORMANCE OBJECTIVES

Performance objectives are the specific evaluation criteria that flow from the overall project goals. The primary goal of this project involves assessing the long-term impacts of ZVI-Clay Soil Mixing, both within and downgradient of a treated source zone. Performance objectives related to assessment of remediation impacts focus on evaluating existing soil and groundwater data, and enhancing the existing data set with high-resolution data, to improve understanding of site processes. A secondary goal involves advancement of cryogenic coring as an effective site characterization tool, via identification of areas for potential improvement in the implementability, efficiency, and cost-effectiveness of the technology. The specific performance objectives, which were developed pursuant to these project goals, are described below.

Performance objectives include:

1. Supplementation of existing remediation performance data with high-resolution data for key parameters,
2. Assessment of biogeochemical conditions in source-zone soils treated with ZVI-Clay Soil Mixing,
3. Generating data that supplements existing remediation performance data and improves understanding of downgradient processes, and
4. Evaluation of cryogenic coring recovery efficiency and production rate.

A summary of performance objectives is provided in Table 1. Additional details regarding each of these objectives are provided in Sections 3.1 to 3.4.

Table 1. Performance Objective Evaluation

Performance Objective	Success Criteria	Results
Performance Objective 1: Produce high-resolution data for key parameters	Data for chlorinated ethylenes, degradation products, and dissolved inorganics at a resolution of at least one sample per foot of soil core; low-*k* zones identified and increased sample frequency implemented	**Success criteria achieved? Yes.** • High-resolution data was generated for TCE and related degradation products, including gaseous compounds. Analytical methods were sufficient for low detection limits (0.010 mg/kg) for key analytes. • Data were generated on 6-in. sample intervals. • Identification of low-*k* zones in cryogenic cores was challenging, due to frost and possible smearing on the core-liner walls. Where they were identified, low-*k* zones were ultimately analyzed at the same high frequency of one sample per 6 in. of core, which was deemed sufficient for the scale of analysis.
Performance Objective 2: Characterize mixed-soil zone biogeochemical conditions	(1) Significant quantity of ZVI particles remain (>0%) and can be demonstrated to still be potentially reactive; (2) extractable quantity of DNA[1]/RNA[2] exists (>0%); (3) reactivity studies can differentiate between reactive/non-reactive zones	**Success criteria achieved? Mixed.** • ZVI identified in mixed-soil zone. • Biological characterization results are mixed, but show areas for possible improvement for future applications. • Reactivity studies suggested continued reactivity potential exists in the treated soil zone.
Performance Objective 3: Develop improved understanding of downgradient treatment processes and performance	Evidence of degradation and contaminant distribution between transmissive and low-k zones	**Success criteria achieved? Yes.** • Comparison of parent compound (TCE) and products indicates active zones. Reactivity and biological assessment indicates ongoing degradation potential on a depth-resolved basis.
Performance Objective 4: Evaluation of cryogenic coring recovery efficiency and production rate.	Soil core recovery: >90% considered successful; reasonable explanation (e.g., cobbles) if recovery is less Amount of soil core collected each day equal to or greater than previous cryo-coring rates (>30 ft/day)	**Success criteria achieved? Mixed.** • Results were generally good, but were mixed in some areas. Excellent recovery was obtained in most natural soil locations. Recovery was limited in the mixed-soil zone, due to the soft soils. Buried wood inhibited recovery in other locations. • Productivity goals were met each day. Daily production rates, based on cored intervals, ranged from 25 to 37.5 ft/day, and averaged 33 ft/day.

Notes:

1 – DNA: Deoxyribonucleic Acid

2 – RNA: Ribonucleic Acid

3.1 PERFORMANCE OBJECTIVE 1: PRODUCE HIGH-RESOLUTION DATA FOR KEY PARAMETERS

Existing remediation performance data at Site 17 consists primarily of groundwater data collected from monitoring wells and soil data collected from sparse intervals. The existing soil and groundwater data (presented subsequently in Section 4.3), suggest that the source zone remediation was generally successful in reducing contaminant concentrations by multiple orders of magnitude, but that relatively low concentrations of contaminant mass persist within the source area; chlorinated compounds also have been detected in recent monitoring events in downgradient monitoring wells.

Interpretation of the remediation performance data, and evaluation of contaminant mass distribution downgradient, can be enhanced via high-resolution data. The need for high-resolution data to improve understanding of subsurface heterogeneity, both in terms of geology and contaminant distribution, has been well documented (e.g., Sale et al. 2013).

For this project, soil cores were collected cryogenically and analyzed at a high resolution to generate comprehensive depth-discrete data. Strategic selection of parameters for high-resolution analysis may provide an enhanced understanding of contaminant distribution and degradation processes. This performance objective was developed with the intent of evaluating the long-term impacts of ZVI-Clay Soil Mixing via collection of high-resolution multi-parameter data.

3.1.1 Data Collected

The analyses conducted in this project were selected based on (a) enhancing current level of understanding regarding contaminant distribution, (b) comparing high-resolution data to existing Site 17 remediation performance-assessment data, and (c) evaluating factors governing long-term fate of contaminant mass that remains at Site 17. Existing site data has focused on perchloroethylene (PCE), TCE, and related degradation intermediates, including *cis*-1,2-dichloroethylene (*c*DCE) and vinyl chloride (VC). In addition, groundwater samples have been analyzed for additional volatile organic compounds (VOCs), dissolved gases (methane, ethane, ethylene), and dissolved ionic species.

For this project, depth-discrete data for chlorinated ethylenes (PCE, TCE, *c*DCE, VC), degradation products (methane, ethane, ethylene), and dissolved inorganic species (iron, anions) was collected.

Supplementary data were also collected for microbial counts, microbial characterization, hydraulic conductivity, ZVI content, and reduction potential.

3.1.2 Interpretation

Success criteria achieved? Yes.

The cryogenic coring and subsequent high-density analysis resulted in high-resolution data for all of the target parameters. Data for TCE and related chlorinated ethylenes was generally produced on a scale of at least one sample per 6 inches of frozen core, with some exceptions occurring where core recovery was limited (addressed under performance objective 4, Section 3.1.4). TCE and related chlorinated ethylenes were adequately preserved and analytical methods were satisfactory to provide results over a wide range of concentrations (typical detections ranged from 0.01 to >1000 mg/kg). In addition to the chlorinated ethylenes, high-resolution data were generated for gaseous products including methane, ethane, ethylene, and acetylene; gaseous product data are essential in determining TCE degradation occurrence and pathways. Data were produced for inorganic constituents including chloride, nitrate, sulfate, and iron. Chloride provides evidence of past reductive dechlorination. Nitrate, sulfate, and iron are useful as redox indicators.

To utilize this high-resolution data to evaluate long-term remediation impacts, parallel-data plots were developed (Section 6.1.1). The parallel-data plots provide a side-by-side comparison of depth-resolved data for several parameters, including geologic logs. The parallel data plots can be used to determine properties that vary with depth, such as transmissive and low-k soil strata; contaminant distribution, transport related parameters (e.g., sorption), and evidence of degradation.

Data plots were also developed to compare the high-resolution C_3 data to groundwater data from adjacent wells (Section 6.1.2). The C_3 data from within the screened depth interval of adjacent monitoring wells generally correlates well with the monitoring well data, collected from a similar time. This suggests that the C_3 technology provides a thorough data set by which the monitoring well data can be enhanced; monitoring well sampling provides a cost-effective method to evaluate temporal trends, while the C_3 technology provides a means to supplement monitoring well data with multi-parameter depth-discrete data.

Following the high-resolution data for multiple parameters, coupled with the positive comparison to existing monitoring well data, this performance objective is considered to have been successfully addressed.

3.2 PERFORMANCE OBJECTIVE 2: CHARACTERIZE MIXED-SOIL ZONE BIOGEOCHEMICAL CONDITIONS

Prior to this project, existing data indicated that peak treated-zone concentrations had been reduced by approximately four and five orders of magnitude in soil and groundwater, respectively, since remediation was completed in 2012. Chlorinated-ethylene concentrations had been reduced by one-or-more orders of magnitude throughout most of the treated zone, but some chlorinated intermediates persisted in the former high-concentration areas within the mixed-soil zone. Questions regarding source-zone treatment include: (a) does the ZVI continue to provide potential reactivity? and (b) what role has biodegradation played in mixed-zone contaminant concentration reductions?

3.2.1 Data Collected

Information collected to complete this assessment include depth-discrete concentration data for chlorinated ethylenes and gaseous products. Supplemental data that supports this performance objective include ZVI content, reactivity, and microbial analyses. Data for chlorinated ethylenes and gaseous products from within the mixed soil zone were generated at a rate of 0.93 samples per foot of cored depth. The sampling resolution was limited, to some extent, by the inhibited recovery from within the mixed soil zone (see Section 6.4).

3.2.2 Interpretation

Success criteria achieved? Mixed.

Prior geochemical data suggest previous degradation of large quantities of chlorinated ethylenes has occurred in the mixed-soil zone, and suggest that conditions are amenable to continued degradation. Elevated chloride concentrations in existing groundwater data from both source-area monitoring wells suggest past reductive dechlorination of chlorinated ethylenes. Both TCE and *c*DCE remain present in soil samples over part of the mixed-soil zone. ZVI remains present in the mixed-soil zone, and reactivity studies confirm the ongoing potential for degradation. Overall, the results suggest that the source zone has been effectively treated, and does not present a substantial threat for ongoing water contamination.

3.3 PERFORMANCE OBJECTIVE 3: DEVELOP IMPROVED UNDERSTANDING OF DOWNGRADIENT TREATMENT PROCESSES AND PERFORMANCE

Treatment of a source area by soil mixing with ZVI and bentonite can affect downgradient soil and groundwater in several ways. The bentonite-induced reduction in hydraulic conductivity, coupled with ZVI-mediated contaminant degradation, can reduce mass loading via groundwater flow into the downgradient plume. The reduction in hydraulic conductivity can have other impacts; for example, a stagnant groundwater zone may persist downgradient of the treated zone in a hydraulic "shadow." The strongly reducing conditions present in the mixed-soil zone may induce reducing conditions downgradient, via diffusion of hydrogen or other reduced species. This performance objective evaluates conditions related to these factors in locations downgradient from the treated-soil zone at Site 17.

The objective is considered to have been successfully achieved if the high-resolution soil-core data can provide additional insights into contaminant distribution and processes occurring downgradient of the treated-soil zone at Site 17. In particular, this performance objective is intended to evaluate the impact of contaminants occurring in low-*k* zones, which may not be represented in groundwater samples from monitoring wells.

3.3.1 Data Collected

A suite of biogeochemical data were collected and analyzed to support this objective. Specific processes of interest include (a) abiotic degradation mediated by natural minerals, (b) microbial activity in low-*k* zones, and (c) role of diffusion in downgradient contaminant longevity following source zone remediation. Data collected in support of these analyses include concentrations of contaminants, degradation products, microbial characterization, and redox indicators.

3.3.2 Interpretation

Success criteria achieved? Yes.

For this objective, the data were interpreted by evaluating redox-sensitive parameters at various locations downgradient of the treated-soil zone. Two existing monitoring wells were evaluated, and four locations were selected for high-resolution characterization to provide transect data that aligned with the monitoring wells. One downgradient location was adjacent to the high-concentration area of the mixed soil zone; other locations were further downgradient and/or in areas that were historically impacted by much smaller amounts of TCE.

The data provide a substantial snapshot of redox conditions, contaminant distribution, and degradation products in downgradient locations. Furthermore, the data are used to support both biological and abiotic degradation processes occurring in the downgradient locations.

Results from one transect of high-resolution soil-core data (DG1), coupled with groundwater data from adjacent monitoring well MW10, suggest that relatively low quantities of chlorinated ethylenes were present in this area, even though these locations are apparently downgradient of the former source zone. Data from monitoring well MW10 are generally consistent with the high-resolution data from nearby soil-core location DG1B. High-resolution data from both soil-core locations (DG1A and DG1B) indicate that contaminant mass within this transect occurs primarily in transmissive zones.

Results from the second data transect (DG2), coupled with monitoring well MW02, present a contaminant distribution profile that is starkly different from transect DG1. Data from monitoring well MW02 contrasts with nearby soil-core location DG2B. The high-resolution data from both locations occurring downgradient in transect DG2 (DG2A and DG2B) indicates substantial contaminant mass occurs within the underlying low-*k* clay aquitard at this location.

Additional data interpretations regarding monitoring-well and high-resolution C_3 data from downgradient locations is presented in Section 6.3.

3.4 PERFORMANCE OBJECTIVE 4: EVALUATE CRYOGENIC CORING RECOVERY EFFICIENCY AND PRODUCTION RATE

A potential advantage of the C_3 technology used for soil core collection as part of this project involves improved recovery of soil core. For the purpose of this analysis, "core recovery" refers to the fraction of the vertical interval that is recovered in a frozen soil core. Freezing of the soil core *in situ* precludes the possibility of gravity- or suction-induced losses of core during the process of retrieval to the surface. To evaluate the potential for improved recovery, soil core recovery data was tracked and reported.

Conversely, a potential limitation the C_3 technology involves the field-production rate, although recent work (prior to this project) has drastically improved productivity to about 26 to 36 feet per day (Kiaalhosseini et al. 2016). Following the procedures developed under recent SERDP projects (ER-1559 and ER-1740), cryogenic coring productivity has advanced to the point where substantial improvements were not expected as part of this project. Rather, the expectations for this project in terms of optimization involved (a) demonstrating that production rates can be obtained in new sites with variable geology, and (b) identifying components of the process where additional improvements may be made.

3.4.1 Data Collected

The data consisted of measured length of each soil core and related depth interval. Recovery is calculated for each core section as the soil-core specimen length divided by the total length of the liner. For this project, all liners were cut to a total length of 30 in. (±1 in., typically).

In terms of field-production rates, daily totals for the length of core collected were recorded, along with the time on site. Additional data collected included time to collect individual cores and time required for various steps in the core-collection process (e.g., time required to freeze core, extract core from the subsurface, and complete handling of core after removal from the subsurface).

3.4.2 Interpretation

Success criteria achieved? Mixed.

As stated in Table 1, a recovery of greater than 90% was considered successful. As discussed in detail in Section 6.4, recovery of 90% or greater was achieved in 36% of core sections.

In fact, recovery of less than 50% was achieved in 33% of cores, all but one of which occurred within the mixed-soil zone. The limited recovery in the mixed soil zone is attributed to the soft soils in the area; advancing the coring tool through the bentonite-mixed soils resulted in "squishing" much of the soil out of the way. Outside of the mixed-soil zone (i.e., in downgradient locations), recovery in some samples was limited due to buried woody debris, which block soil from entering the continuous core sampler. From these observations, the limited recovery in Site 17 samples is not attributed to cryogenic collection, *per se*.

In summary, although recovery of 90% or greater was not achieved in the majority of samples, this performance objective is considered to have been addressed, as explanations are available for core sections with <90% recovery. Issues associated with traditional coring, such as suction, flowing sands, and pore-fluid drainage, were not encountered during soil-coring activities at Site 17.

The cryogenic coring production goals for the project were met. The productivity data were interpreted by comparing core production rates to previous rates. The goal was to meet or exceed the previous production rates of about 30 feet per day. Causes for delays that occurred during the field core collection were also evaluated to identify possibilities for future improvements.

The general productivity goals were met. Over the three days of cryogenic coring at Site 17, sampled intervals ranged from 25 to 37.5 ft and averaged 33 ft/day. Minor delays were encountered due to (a) coring equipment freezing downhole, (b) freezing or binding of the core sample in barrel, and (c) running out of LN in the vicinity of sampling. These are discussed in more detail in Section 8.0.

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4.0 DEMONSTRATION SITE DESCRIPTION

The DoD site selected for this post-remediation performance assessment is Site 17, NSFIH, Maryland. Maps showing the site location and vicinity are presented on Figure 6 and Figure 7, respectively. Source zone remediation was conducted at this location in November 2012 using soil-mixing techniques to deliver ZVI for *in situ* chemical reduction. This section provides a detailed site description, remediation history, and available data.

4.1 SITE LOCATION AND HISTORY

Historical use of the NSFIH facility includes a variety of gun testing, ordinance production, and a variety of related chemistry and engineering activities (NSFIH 2015). Within the greater NSFIH facility, Site 17 was used for metal part processing and storage in the 1960s and 1970s (CH2M HILL 2008). Associated with this historical site use, the primary contaminant present at Site 17 is TCE; products of natural TCE degradation, primarily *c*DCE and VC, were also present in the subsurface prior to remediation activities. Pre-remediation TCE concentrations indicated the likely presence of DNAPL over a portion of the site.

ZVI-Clay soil mixing was conducted at Site 17 to treat the TCE source zone (details are provided in Section 4.2.1). The ZVI-Clay Soil Mixing remediation is the focal point for the current project. Another Environmental Security Technology Certification Program (ESTCP) project is currently ongoing at Site 17; a Contaminant Flux Reduction Barrier (CFRB) was installed by Groundwater Services Inc. (GSI) in the summer of 2015 (GSI 2015). Ultimately, the goal of the remediation activities at Site 17 is to transition into a Monitored Natural Attenuation (MNA) phase (CH2M HILL 2013).

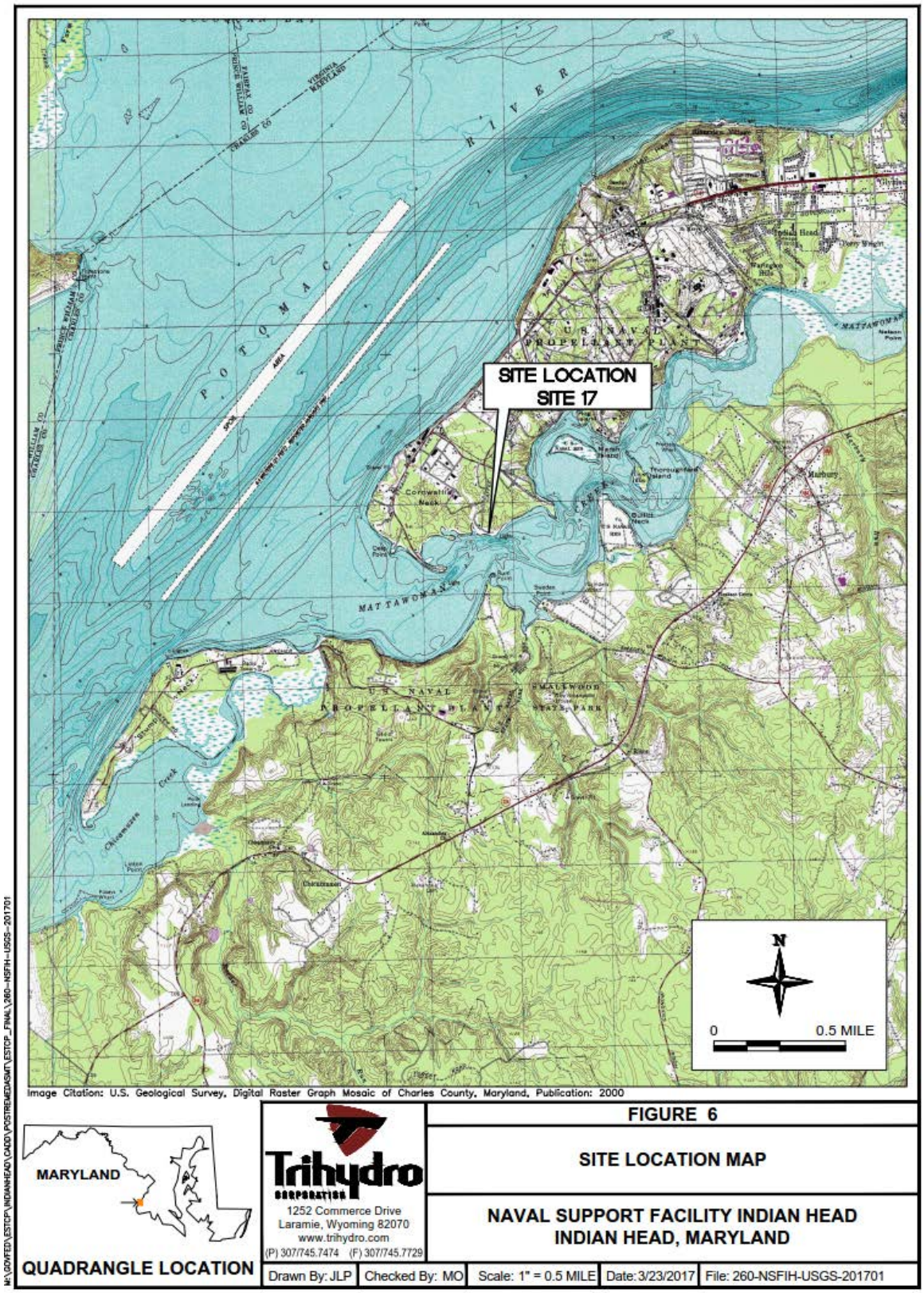

Figure 6. Site Location Map.

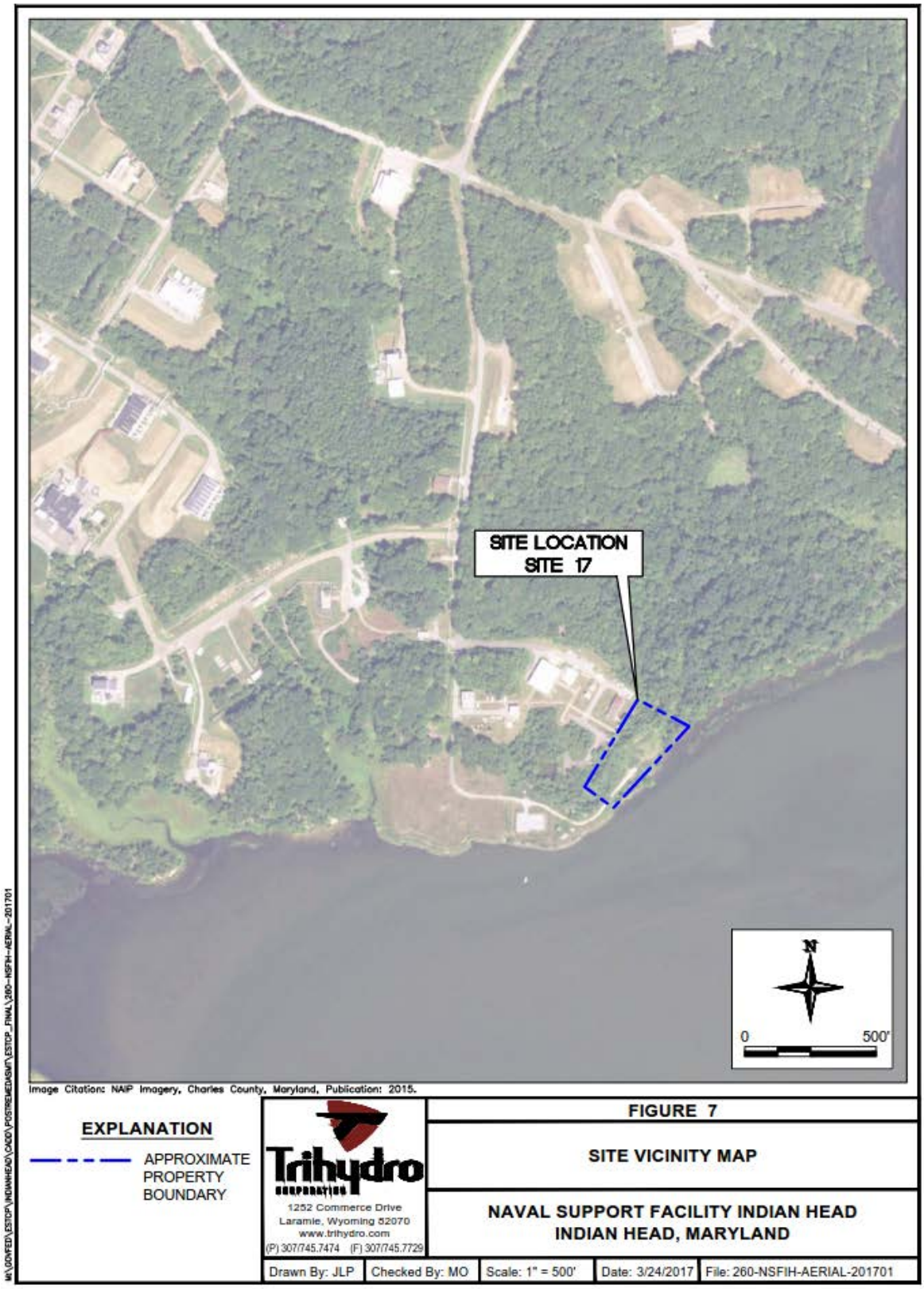

Figure 7. Site Vicinity Map.

4.1.1 ZVI-Clay Soil Mixing

ZVI-Clay Soil Mixing was completed at Site 17 in November 2012 (CH2M HILL 2013), approximately 4 years prior to the field core-collection activities described herein. The remediation was conducted using soil-mixing equipment (Figure 8) to homogenize soils in the targeted treatment zone. During mixing, ZVI and bentonite were delivered via ports in the soil-mixing tool. ZVI is a reductant, which mediates degradation of chlorinated solvents. Bentonite was added to reduce hydraulic conductivity. The combination of ZVI-mediated contaminant degradation and bentonite-induced reduction in groundwater flow rate was intended to result in contaminant-flux reduction by multiple orders of magnitude, as has been documented for ZVI-Clay applications (e.g., Olson and Sale 2015).

Figure 8. Soil Mixing Equipment at Site 17 (CH2M HILL 2013).

Soil Mixing Implementation. Implementation of ZVI-Clay Soil Mixing at Site 17 required two weeks for completion. The targeted mixing zone at Site 17 is shown in Figure 9. Within the target treatment zone, soils were mixed from depths of 2 to 18 ft bgs, and ZVI was injected at depths of 8 to 18 ft bgs. The total mixed volume of soils was about 1300 yd^3. Mixing was completed by Geosolutions, Inc. (Pittsburgh, PA). Mixing was completed using a 9-foot diameter mixing tool; 70 overlapping mixed columns were installed to ensure treatment of the entire target treatment zone.

All of the target treatment-zone soils were mixed with a target amount of at least 1% ZVI. Three of the mixed-soil columns (shown in Figure 9), which were located in the portion of the site that was inferred to contain DNAPL, were admixed with excess ZVI that was diverted from column locations with significant overlap. To ensure that target ZVI quantities were being met, soil samples were collected during mixing for Quality Assurance/Quality Control (QA/QC) testing. The ZVI-content QA/QC samples were collected from 10 of the 70 mixed-soil columns at three depths (30 total QA/QC samples), ranging from 8 to 15 ft bgs. The ZVI content was evaluated via magnetic separation techniques. Summary statistics on the measured ZVI content in QA/QC samples are shown (Table 2) for the standard-ZVI area and for the excess-ZVI area.

Results indicated that all samples met or exceeded the target ZVI amount of 1%. In total, mixing activities required 30 tons of bentonite and 31 tons of ZVI (CH2M HILL 2013). The homogeneous geology achieved via soil mixing is illustrated in Appendix B (geologic cross sections and logs) and further described in Section 4.2.

Table 2. QA/QC ZVI Content Summary Statistics

ZVI Content (%)	Standard-ZVI Area	Excess-ZVI Area
Average	1.6	3.5
Minimum	1.0	2.9
Median	1.7	3.6
Maximum	2.9	4.3
Number of columns sampled	8	2
Number of QA/QC samples	24	6

Remediation Performance Monitoring. Routine performance monitoring consisted of baseline (pre-mixing) data and post-mixing sampling events conducted through 36 months after mixing was completed (Section 4.3). Baseline sampling was conducted in October 2012, approximately one month prior to source-zone remediation. The baseline sampling event included collection of soil and groundwater samples, from locations within and outside of the target mixing zone. Temporary borings were installed within the target mixing zone at three locations (DP69, DP70, and DP71) using direct push tooling; groundwater samples were collected from these borings using temporary polyvinyl chloride (PVC) piezometers, and soil samples were collected from the depth interval of highest contamination (based on photoionization detector readings). Five groundwater monitoring wells located outside of the target mixing zone (MW02, MW03, MW04, MW06, and MW09) were also sampled as part of the baseline characterization event.

Post-remediation sampling events were conducted at approximate times of 7, 9, 12, 15, 18, 24, 27, 33, 36, and 40 months after mixing was complete. Most of the post-remediation monitoring has comprised collection of groundwater and soil samples from locations within and outside of the mixed-soil zone. Two permanent monitoring wells (MW07 and MW08) were installed in the treated-soil zone at approximately 12 months.

Most of the groundwater and soil samples were analyzed for VOCs (TCE, cDCE, VC). Monitoring-well based groundwater samples were also analyzed for gaseous products (methane, ethane, and ethylene) and inorganic parameters (chloride, nitrate, nitrite, and sulfate). Some groundwater samples were also analyzed for volatile fatty acids. Select soil and groundwater samples were analyzed for microbial community profile.

Results through 12 months were presented in the Site 17 Annual Report (CH2M HILL 2014); results through 24 months were presented in the Site 17 Year 2 Post-Soil Mixing Monitoring Report (CH2M HILL 2015); more recent data were provided to the project team directly by CH2M HILL. Data plots for existing groundwater and soil data are provided in Appendices C and D, respectively.

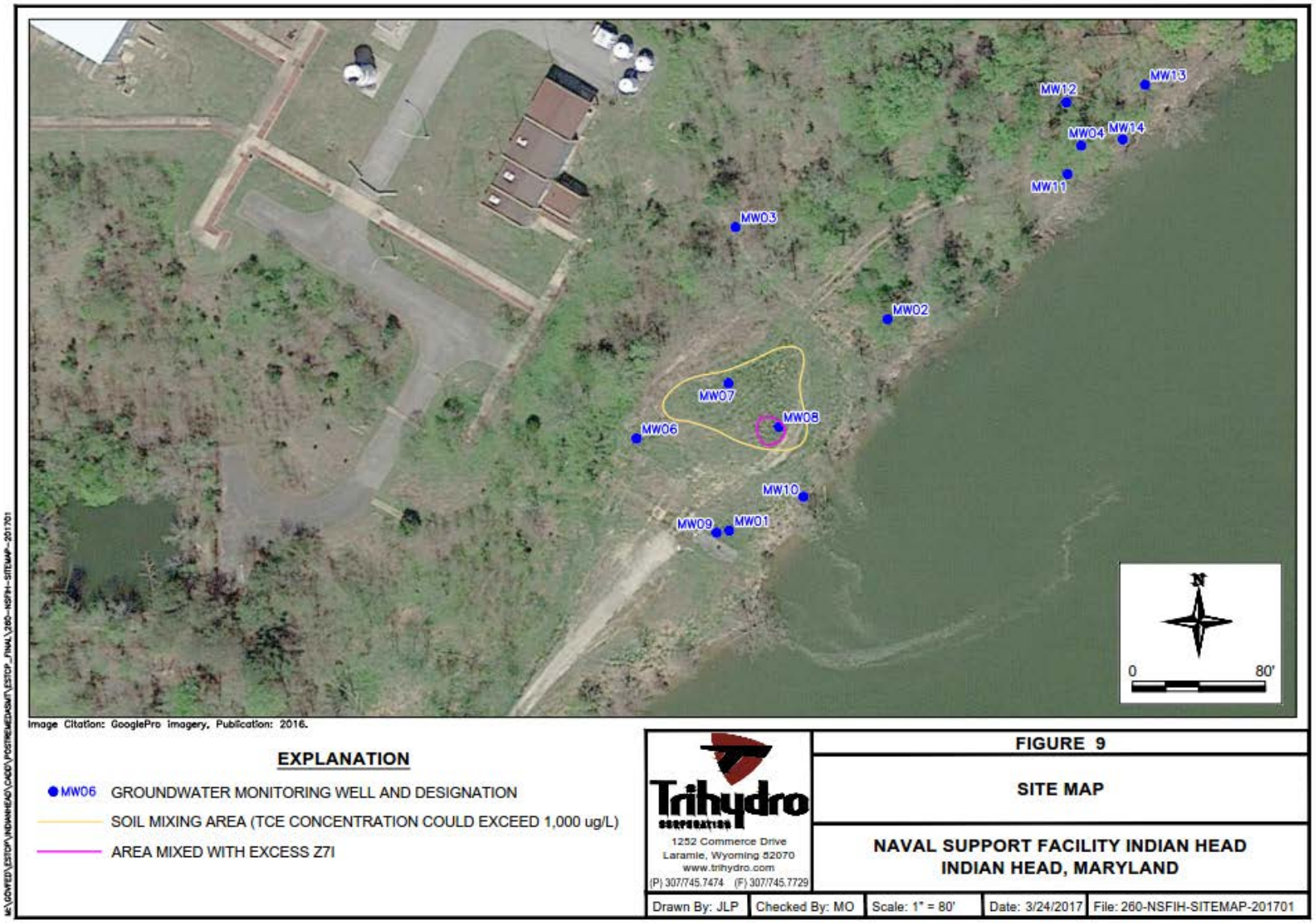

Figure 9. Site Map with Target Soil-mixing Remediation Zone (after CH2M HILL 2013).

4.1.2 Contaminant Flux Reduction Barrier

Another ESTCP demonstration project (ER-201328) is ongoing at Site 17, to evaluate the performance of a CFRB. The location of the CFRB is shown in Figure 10. This ESTCP demonstration is being conducted to evaluate implementation of an upgradient groundwater-flow barrier, coupled with enhanced biological degradation downgradient of the barrier. The goal of the CFRB demonstration is to demonstrate flux reduction and source-zone contaminant mass removal in a relatively passive manner.

The performance evaluation of ZVI-Clay Soil Mixing reported herein was unrelated to the CFRB. Based on the location of the CFRB, the barrier was not expected to influence the groundwater characteristics or flow patterns in the vicinity of the cryogenic coring locations.

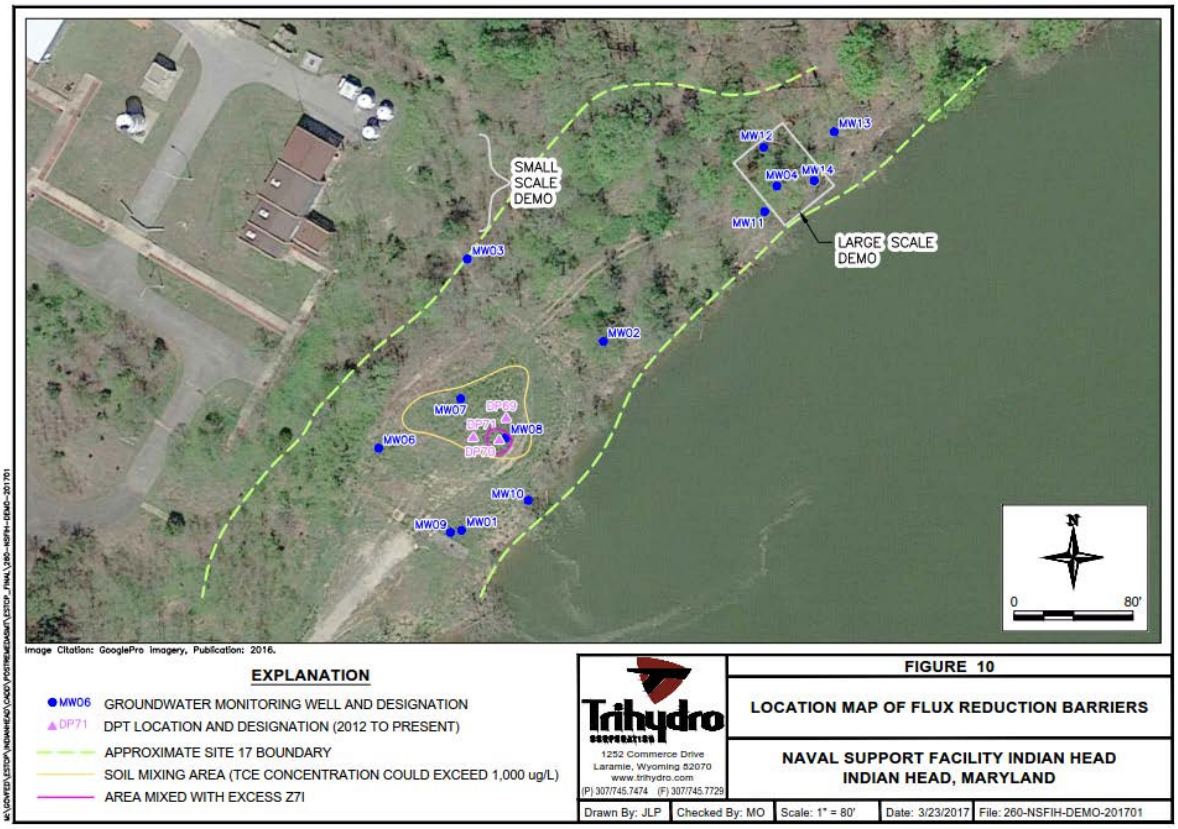

Figure 10. Location Map of Flux Reduction Barriers (after GSI 2015).

4.2 SITE GEOLOGY/HYDROGEOLOGY

4.2.1 SITE 17 GEOLOGY

Site geology had been previously characterized using borehole logs and direct-push electrical conductivity measurements (CH2M HILL 2008). The geology consists of a mixture of silty sand/sandy silt to a depth of about 10 feet, overlying subsequent silt and clay layers. The underlying silt/clay functions as an aquitard. The depth to the aquitard ranges from about 12 to 18 feet across the area of interest at Site 17. Geologic cross sections are provided (Appendix B).

Within the former source zone, the geology has been modified via soil mixing, which occurred to a depth of approximately 18 feet below ground surface (ft bgs). The ZVI-Clay Soil Mixing involved use of an auger mixing tool to homogenize soils and achieve uniform delivery of ZVI and bentonite. Key properties of the mixed-zone soils include the following: (a) heterogeneous soil layers are largely removed, due to homogenization achieved by mixing; (b) bentonite is distributed throughout, which may affect soil properties including hydraulic conductivity and load-bearing capacity; (c) excess water is often added during mixing, and may take an extended period (months to years) to drain from the low-*k* mixed soils. Soil properties may change in the first few months to years after mixing, as settlement occurs.

4.2.2 SITE 17 HYDROGEOLOGY

Previous investigations have concluded that the hydraulic gradient was approximately 0.04 ft/ft in a southeasterly direction, with groundwater ultimately being discharged into Mattawoman Creek (CH2M HILL 2008). The time-variation of hydraulic gradient, calculated based on recent data (2012 to 2015) is shown on rose-plots on Figure 11. The post-mixing direction and magnitude of the hydraulic gradient are similar to that estimated prior to soil mixing (CH2M HILL 2008). This suggests that general flow conditions have been restored in the period since mixing was completed.

Slug tests conducted by CH2M HILL (2008) were conducted to estimated hydraulic conductivity values at Site 17. Estimated hydraulic conductivity values of the upper sand/silt layer ranged from 0.9 to 8.3 ft/day (3.2×10^{-4} to 3.0×10^{-3} cm/sec); the hydraulic conductivity of the underlying clay was measured at 6.5×10^{-4} ft/day (2.3×10^{-7} cm/sec). The hydraulic conductivity values of mixed-zone soils is also likely to have been affected by the soil mixing with bentonite; reduction in hydraulic conductivity by one (or more) order(s) of magnitude is expected after applications of soil mixing with bentonite.

CH2M HILL (2008) also investigated the tidal influence at Site 17. Surface water fluctuations in Mattawoman Creek, directly adjacent to the site, are approximately 1.5 ft. Continuous measurements, collected in inland monitoring wells to evaluate the influence of tidal fluctuations on the water table, indicated fluctuations of 0.1 ft or less. The study concluded that tidal fluctuations had little effect on site groundwater patterns.

Travel time analysis, based on the preceding hydraulic data, is presented in Table 3. Travel times are based on travel from the mixed-soil zone to the indicated monitoring well.

Table 3. Travel Time Calculations

Monitoring Well	Distance (ft)	Hydraulic Conductivity Basis	Hydraulic Conductivity (ft/d)*	Gradient (ft/ft)	Effective Porosity	Calculated Seepage Velocity (ft/d)	Time (d)
MW02	70	minimum	4.5	0.04	0.4	0.45	155.6
	70	average	6.1	0.04	0.4	0.61	114.8
	70	maximum	9.2	0.04	0.4	0.92	76.1
MW10	40	minimum	4.4	0.04	0.4	0.44	90.9
	40	average	8.3	0.04	0.4	0.83	48.2
	40	maximum	14.4	0.04	0.4	1.44	27.8

* From CH2M HILL (2008)

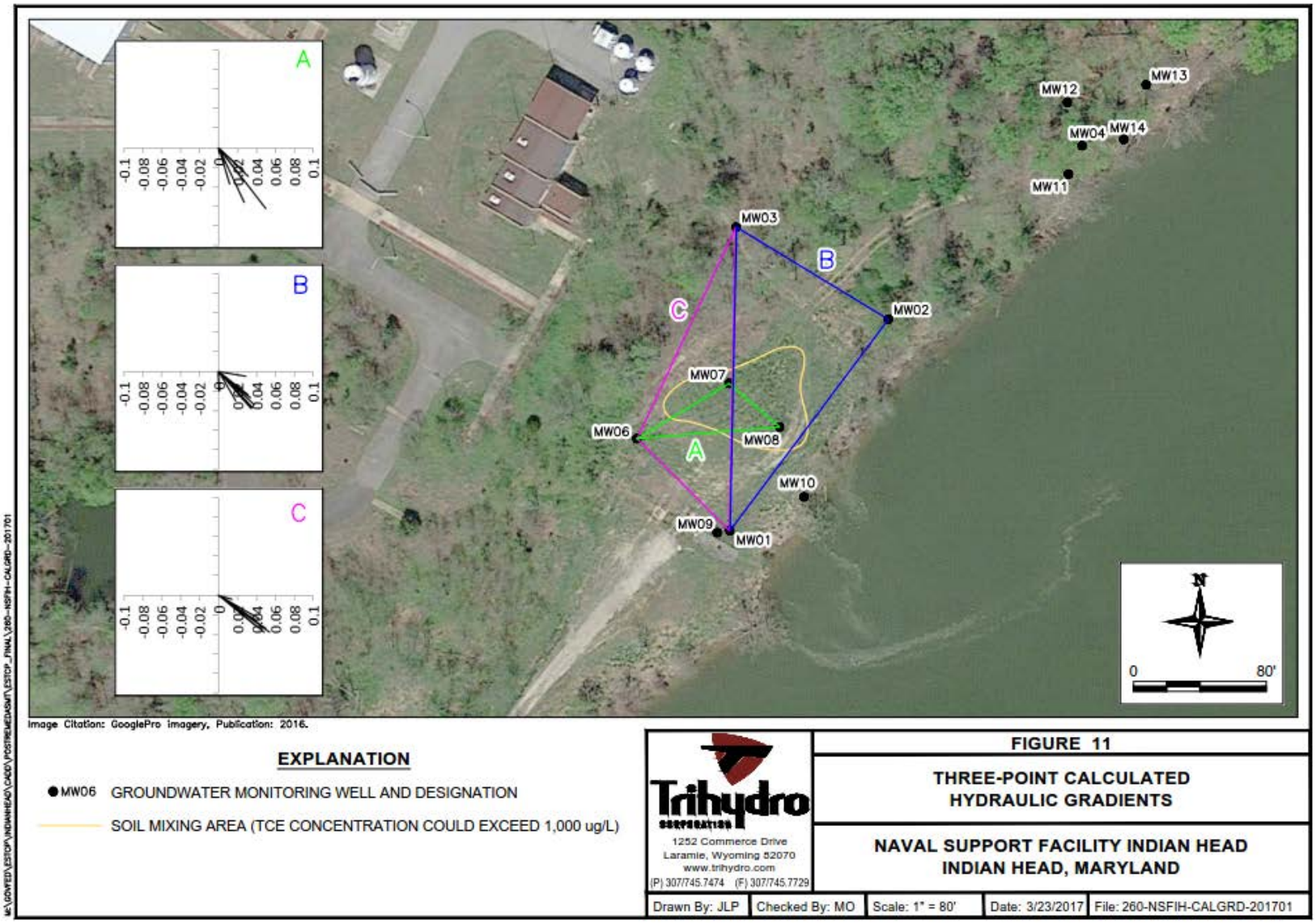

Figure 11. Three-point Calculated Hydraulic Gradients.

4.3 CONTAMINANT DISTRIBUTION

Existing remediation performance data indicate that the contaminant distribution was affected by the ZVI-Clay Soil Mixing remediation. Charts showing detailed concentration data versus time for groundwater and soils are shown in Appendices C and D, respectively. Data are shown for VOCs, gaseous products, and select inorganic analytes. Concentration contour maps for TCE, *c*DCE and VC, showing both baseline (i.e., before soil mixing remediation was implemented) and 24-month post-mixing data, are also shown in CH2M HILL (2015). Implications of the change in contaminant distribution, imposed via soil mixing remediation, are discussed in the following section (Section 4.4, Conceptual Site Model).

4.3.1 Pre-Remediation Contaminant Distribution

The primary parent compound was TCE. Degradation products including *c*DCE and VC were also present. The approximate boundary of the source area, which was defined as the area with concentrations greater than 1 mg/L, is shown in Figure 9. Pre-mixing concentrations as high as 820 mg/L for TCE were detected, providing strong evidence that TCE DNAPL was present in portions the source zone, primarily in the southeast portion of the source zone. Degradation products including *c*DCE and VC were detected in direct-push groundwater samples at concentrations up to 220 and 80 mg/L, respectively (CH2M HILL 2008).

4.3.2 Remediation Performance

Remediation performance data for groundwater and soils are shown in Figure 12 and Figure 13, respectively. Detailed concentration data (VOCs, gaseous products, and select inorganic analytes) versus time for groundwater and soils are shown in Appendices C and D, respectively.

A comparison of pre- and post-mixing data indicates that substantial concentration reductions occurred. Peak dissolved-TCE concentrations were reduced from 1,500 to 0.015 mg/L. Intermediate compounds (*c*DCE and VC) increased in the 12 months after mixing was complete, but have subsequently declined. Ultimately, *c*DCE concentrations have declined from peak pre-mixing levels of 27 mg/L to 0.18 mg/L in 24 months. VC concentrations have declined from peak pre-mixing levels of 5.0 mg/L to 0.25 mg/L over 24 months. As a result of the remediation, the "source area" no longer exists; the source area was defined as the zone in which contaminant concentrations exceed 1.0 mg/L, and all concentrations have been reduced to levels below this threshold (CH2M HILL 2015). Where contamination persists in the treated soil zone, contaminants should remain isolated from surrounding groundwater flow due to reduction in hydraulic conductivity. Within the mixed-soil zone, continued degradation of contaminants is expected (evaluating this is one of the goals of the present project).

Outside of the treated-soil zone, impacts of the remediation are not readily apparent in monitoring data. The lateral extent of the plume exceeding the site remediation goal of 0.005 mg/L did not change significantly. Temporary increases in TCE degradation-product concentrations were noted in MW02, as high as 8.7 and 2.5 mg/L (for cDCE and VC, respectively) within 20 months after soil mixing was complete; these increases may be attributed to reducing conditions generated by the ZVI-Clay Soil Mixing. The impact of ZVI-Clay Soil Mixing on degradation processes in the adjacent untreated materials has typically only been evaluated indirectly, i.e., through measurement of degradation products.

Overall, the remediation was considered as being successful, and resulted in a reduction of peak dissolved-phase TCE concentration of greater than five orders of magnitude; peak soil concentration have been reduced by greater than four orders of magnitude (CH2M HILL 2015) (see Section 4.4 for more detail). According to CH2M HILL (2015), the ZVI-Clay Soil Mixing at Site 17 "has been effective in reducing the TCE, DCE, and VC concentrations to levels below the [site remediation goals] within the source zone area. TCE, DCE, and VC concentrations have also decreased significantly in the area outside the source zone area as a result of reductions in the source area concentrations." Transition to a long-term monitoring phase is currently under evaluation.

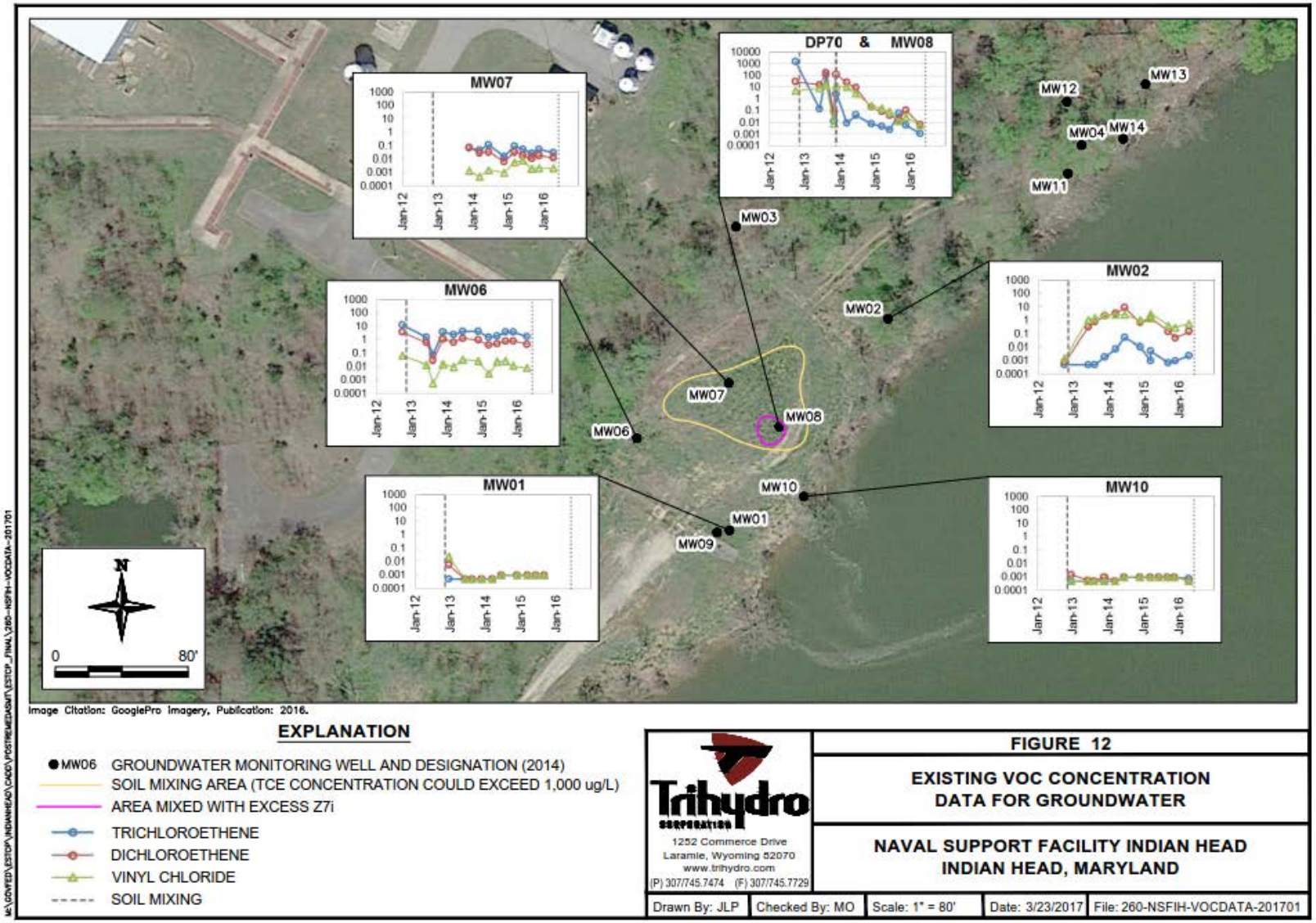

Figure 12. Existing VOC Concentration Data for Groundwater.

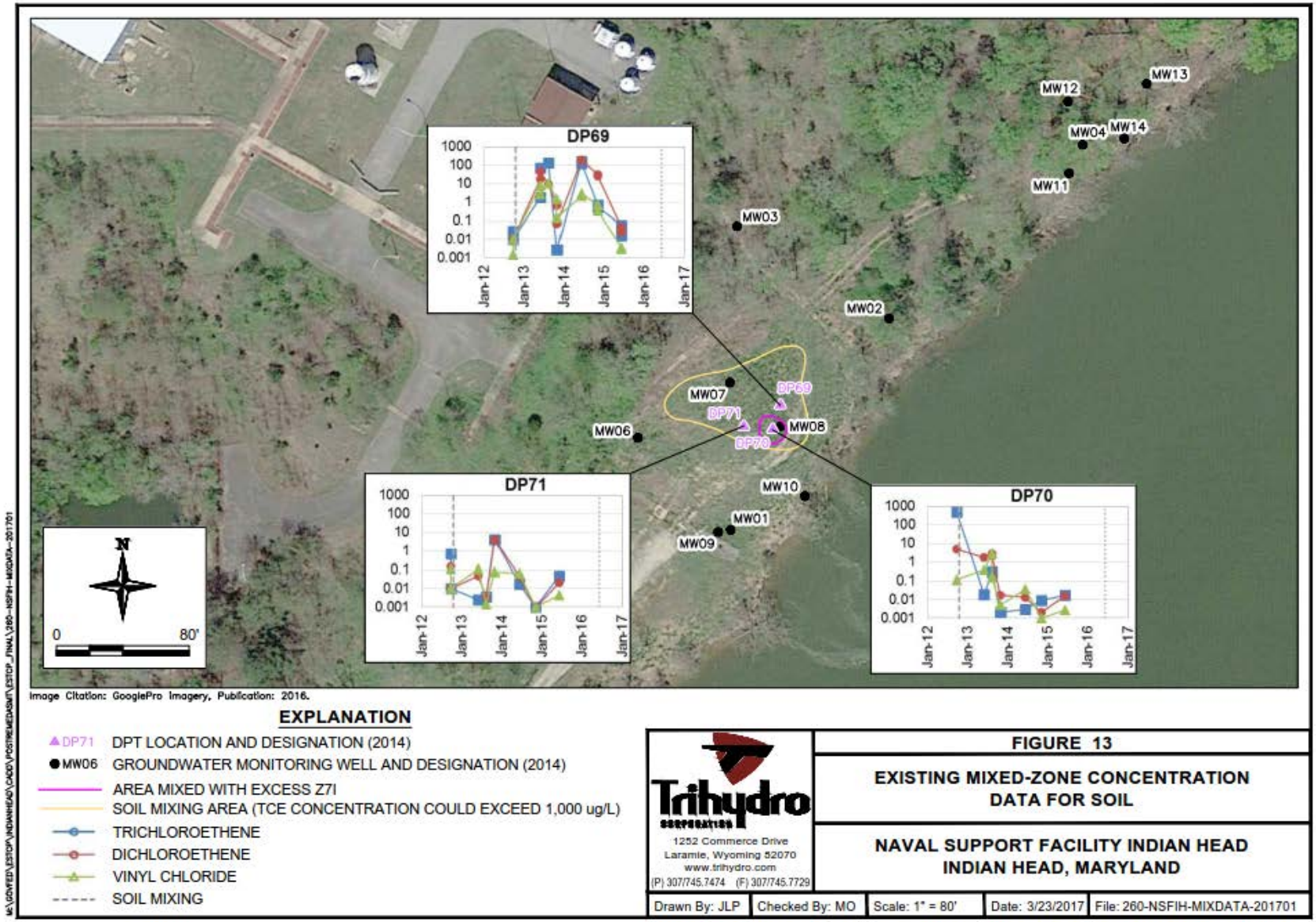

Figure 13. Existing Mixed-zone Concentration Data for Soil.

4.4 CONCEPTUAL SITE MODEL

This section develops a CSM for the expected geochemical conditions at Site 17, four years after source-zone treatment with ZVI-Clay Soil Mixing was completed. This CSM is developed based on existing site data and identifies data needs, some of which form the basis for performance objectives of this project, described in Section 3.0. To develop this CSM, general inferences and observations for soils treated via ZVI-Clay Soil Mixing are presented in the following subsection (Section 4.4.1). Subsequent sections describe how these general expectations correspond with observations at Site 17, both within the mixed soil zone (Section 4.4.1) and downgradient (Section 4.4.2).

4.4.1 Expected Conditions for ZVI-Clay Soil Mixing

Unlike many remediation technologies, the ZVI-Clay Soil Mixing remediation technology affects both the geology and contaminant distribution. Through implementation of soil mixing, several changes are rendered:

- Within the mixed-soil zone, interbedded soil strata of varying permeability are transformed into a single, relatively uniform low-*k* soil zone;
- Within the mixed-soil zone, contaminants that have been subject to natural processes (e.g., initial distribution upon release, subsequent advective and diffusive transport, sorption, and degradation) for extended periods (e.g., decades) are re-distributed and brought into close contact with reactive media; and
- Within the mixed-soil zone, conditions are amendable to contaminant degradation for some time (at least three years, as suggested by Olson et al. 2012) after mixing, the duration of which is a function of several factors including initial contaminant mass, quantity of ZVI, geochemical conditions, and competing reactants.

Inferred post-mixing groundwater flow patterns are shown on Figure 14. The patterns indicate that groundwater tends to bypass the mixed soil zone, which is consistent with observations from previous ZVI-Clay Soil Mixing projects (e.g., Olson et al. 2012). Flow is likely to persist within the treated soil zone, but at a reduced rate due to reduction in hydraulic conductivity.

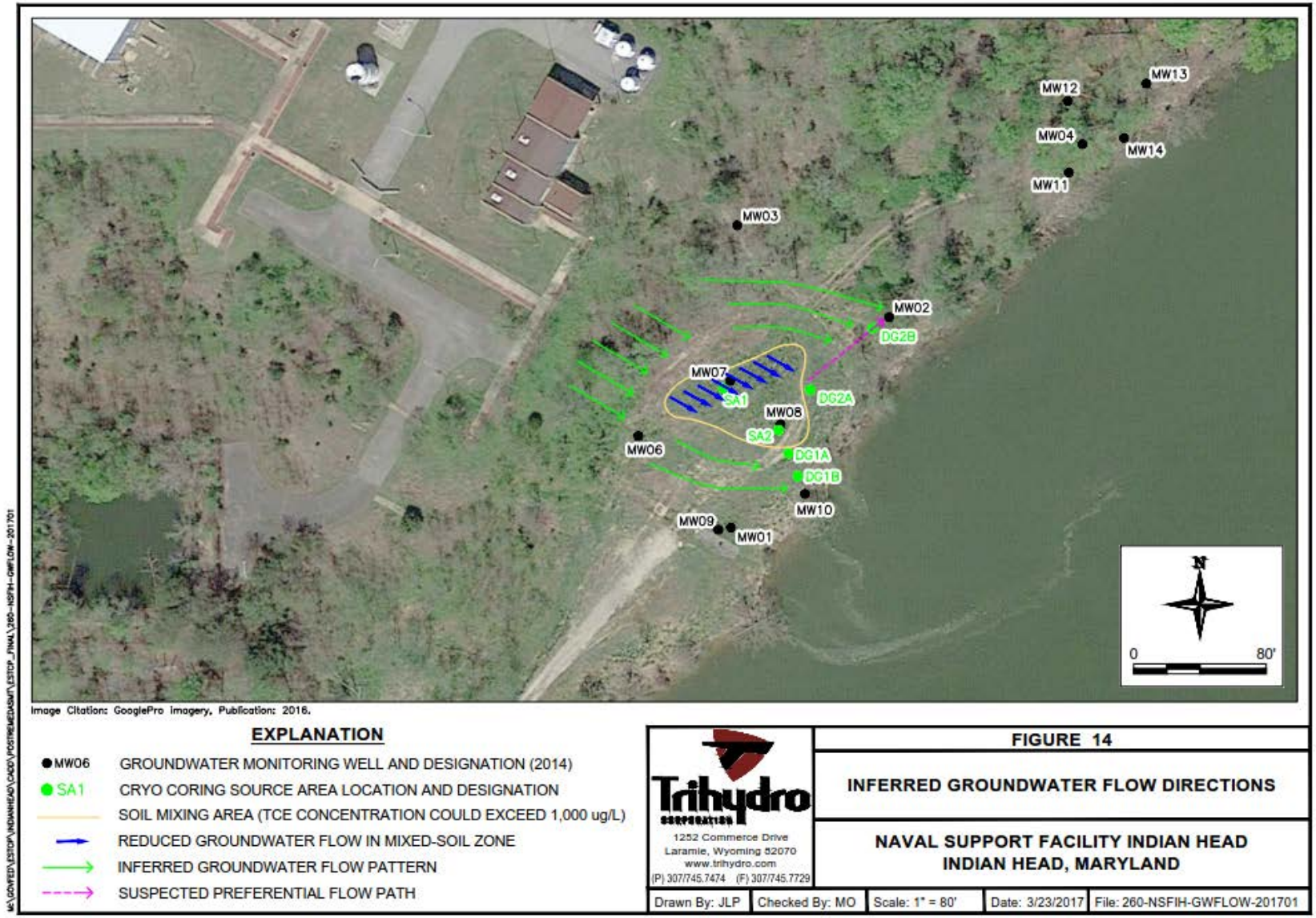

Figure 14. Inferred Groundwater Flow Directions.

Following implementation of ZVI-Clay Soil Mixing, some changes imposed on the treated-soil zone are permanent, and others transient. The geologic/hydrogeologic changes to the mixed zone, which include homogenization and permeability reduction, are expected to be permanent. Post-remediation changes to contaminant mass are likely to have both transitory and permanent aspects. The degradation of contaminant mass is a transient process that occurs in the initial period (months to years) after mixing, while active ZVI-mediated degradation persists. During the active-degradation period, ZVI-mediated degradation of TCE is expected to follow abiotic pathways that minimize formation of DCE isomers and VC, instead forming chlorinated acetylenes (Olson and Sale 2015). Eventually, one or both of the reaction constituents (i.e., ZVI or the readily available portion of contaminant mass) become consumed, after which a new semi-stable condition may prevail. Ultimately, the degradation of contaminant mass constitutes a permanent change to the treated zone.

The geochemical alterations imposed by ZVI-Clay Soil Mixing are also likely to affect conditions in untreated soils outside of the mixed-soil zone. The following flow generalizations are based on groundwater flow modeling of hypothetical mixed-soil zones (Olson 2014). Remediation effects are likely to be apparent both upgradient and downgradient of the treated-soil zone. Upgradient, groundwater flow lines may diverge around the low-*k* mixed-soil zone. Downgradient of the mixed-soil zone, a hydraulic flow "shadow" may become apparent near the mixed-soil body, where groundwater flow is effectively blocked by the imposed low-*k* soil body. Further downgradient, groundwater flow patterns may converge, approaching natural pre-mixing conditions.

The downgradient contaminant mass distribution is also likely to be affected by the ZVI-Clay Soil Mixing technology. Untreated soils near the mixed-soil zone may contain relatively high contaminant concentrations, especially in locations that have been exposed to dissolved-phase discharge from a DNAPL source for extended periods. After implementation of soil mixing, contaminant mass occurring near the source zone may be isolated from groundwater flux, due to the hydraulic shadow mentioned previously. Downgradient soils may also be exposed to strongly reducing groundwater, emanating from the ZVI-treated soil zone.

Further downgradient in the plume, the source-zone removal effects documented by Chapman and Parker (2005) and Sale et al. (2008) are likely to predominate. The ZVI-Clay Soil Mixing technology offers the potential for effective source removal, by combining groundwater flux reduction with contaminant degradation. Source removal is likely to reduce the influx of dissolved-phase contaminant mass into the plume, initiating release of contaminant mass from storage (i.e., via desorption and back diffusion). Thus, in plumes downgradient of source zones remediated via ZVI-Clay Soil Mixing, the long-term concentration distribution may be controlled by several interacting processes including desorption, back-diffusion, and degradation.

Contaminant degradation occurring within and downgradient of treated-soil zones is likely to reflect a combination of biological and abiotic degradation processes. The biological and abiotic degradation pathways for chlorinated ethylenes are described in detail by several researchers (e.g., Arnold and Roberts 2000, Brown et al. 2009, Cox 2012, Chen et al. 2014, He et al. 2015, Whiting et al. 2014), but findings presented by Brown et al. (2009) are summarized here. Biological degradation of chlorinated ethylenes typically follows a stepwise hydrogenolysis pathway: PCE → TCE → DCE isomers (primarily *c*DCE) → VC → ethylene.

Abiotic degradation tends to follow a β-elimination pathway that tends to bypass accumulation of chlorinated intermediates, instead forming chloroacetylenes that are subsequently reduced (via hydrogenolysis) to ethane via the following sequence: chloroacetylene → acetylene → ethylene → ethane. During the period of active degradation, ZVI-mediated (abiotic) degradation patterns for chlorinated ethylenes are likely to prevail within the treated-soil zone. Downgradient of a treated soil zone, both biological and abiotic processes may occur to varying extents, depending on site-specific factors including geochemistry and redox conditions.

Research has shown that chloroacetylenes and acetylene are only formed in measurable quantities via abiotic degradation (e.g., He et al. 2015). Of these, chloroacetylenes are highly unstable and difficult to quantify in environmental samples, but acetylene can be quantified using standard analytical techniques (e.g., EPA Method RSK-175). Acetylene is also readily degraded to ethylene, thus acetylene is likely to be detected only in the presence of active abiotic degradation of TCE or *c*DCE. Ethylene is an intermediate compound, formed via biological and abiotic pathways, and ethane is the end-product of this sequence. Thus, ethylene provides stronger evidence of ongoing degradation, whereas ethane may be a relic of past or upgradient degradation.

4.4.2 Site 17 Biogeochemistry: Within the Mixed-Soil Zone

Soil mixing in Site 17 was completed in 2012, approximately four years prior to the performance assessment work described herein. Within the treated soil zone, the homogeneity of the treated-soil zone at Site 17 is documented in geologic logs pertaining to wells MW07 and MW08, which were installed in the mixed-soil zone about one year after soil mixing was complete (CH2M HILL 2014). The treated-zone soils in both well logs was described as "clayey silt"; by comparison, well-logs from locations outside of the treated-soil zone (for example, MW10, as shown in Appendix B) indicated substantial heterogeneity, comprising interbedded sandy-clay and clayey-silt media. The contrast between treated-zone and non-treated monitoring well logs confirms the homogenization imposed via soil mixing.

The effects of treatment on groundwater and soil concentrations (shown in Appendices C and D, respectively) suggest that most of the ZVI-mediated degradation in the treated-soil zone occurred within the two years after treatment. In groundwater data, which is based primarily on long-screen monitoring wells (screen length = 15 ft), peak TCE concentrations had been reduced by five orders of magnitude. Relatively low (<0.03 mg/L) concentrations of TCE, *c*DCE and VC have continued to be detected in source-area wells MW07 and MW08 (Figure 12). The degradation trends (Section 4.3.2) were generally consistent with abiotic degradation, but biological processes cannot be ruled out given available data, since the existing groundwater samples were not analyzed for acetylene. Elevated levels of degradation products, including ethylene and chloride, provide additional evidence that past reduction of chlorinated ethylenes has occurred.

Existing soil concentration data is based on direct-push soil samples collected from relatively sparse depth intervals. Samples have been repeatedly collected, on an approximate annual basis, from three general locations within the treated-soil zone. In one of these location (DP70), a consistent degradation trend as observed, primarily in the first 24 months after remediation was completed.

Soil concentrations have fluctuated in some source-area locations, which may be attributed to some heterogeneity in post-mixing distribution (either in ZVI content or contaminant mass), or variable depths at which soil samples have been collected over time (CH2M HILL 2015). In the most recent sampling event (April 2015), maximum concentration of TCE, *c*DCE, and VC in soils were 0.049, 0.021, and 0.004 mg/kg, respectively. The most recent trends suggest that total chlorinated ethyelenes are declining in DP69, stable in DP70, and increasing in DP71. Thus, although soil concentrations are substantially reduced from pre-treatment levels, uncertain trends have persisted.

Following this CSM description of the source area, remaining uncertainties at Site 17 involve fate of contaminant mass remaining in the treated zone, degree of homogeneity within the treated zone, and potential for ongoing degradation (either abiotic or biological) of chlorinated ethylenes. In addition, data for acetylene may help to resolve abiotic versus biological degradation pathways.

4.4.3 Site 17 Biogeochemistry: Downgradient of the Mixed-Soil Zone

The natural geology at Site 17 suggests a reasonably high degree of heterogeneity (described in Section 4.2.1). Previously measured hydraulic conductivity testing results suggest that transmissive and low-*k* zone exist at Site 17 (Section 4.2.2), with hydraulic conductivity values ranging over multiple orders of magnitude. A key feature of Site 17 geology involves the underlying clay aquitard.

After soil mixing with ZVI and bentonite, the reduced permeability of the treated-soil zone at Site 17 is likely to affect downgradient groundwater flow patterns, as described previously. General expectations include (a) groundwater flow lines that preferentially bypass the treated soil zone and (b) a flow "shadow" immediately downgradient of the mixed-soil body, where groundwater flow is limited. Existing hydraulic data are insufficient to directly evaluate these theoretical flow patterns at Site 17. However, these general observations may provide context for existing and future data evaluation.

Downgradient groundwater quality impacts of ZVI-Clay Soil Mixing are assessed based on data from monitoring wells MW02 and MW10. Monitoring well MW02 does not appear to be directly downgradient of the treated zone (Figure 14), but appears to have been affected by the remediation, as transient increases in *c*DCE, VC, ethylene, and ethane occurred over a period of one to two years after soil mixing was complete; this suggests a preferential flow path may exist. Concentrations in groundwater samples from MW02 have subsequently followed a declining trend, reaching their lowest measured values for TCE (0.003 mg/L), *c*DCE (0.13 mg/L), and VC (0.56 mg/L) in April 2016. Conversely, monitoring well MW10 appears to have been relatively unaffected by the former source zone and remediation activities; TCE, *c*DCE, and VC have all remained at concentrations less than 0.005 mg/L since remediation was completed. Overall, these groundwater data suggest that the only minor impacts of chlorinated ethylenes are present downgradient of the treated soil zone. However, the potential of contaminant presence in low-*k* zones may be underrepresented by monitoring-well based data.

The existing Site 17 soil and groundwater data are adequate to determine whether remediation performance is meeting performance goals. However, certain aspects of downgradient response to source removal may not be clear based on long-screen monitoring well data provided by monitoring wells such as MW02 and MW10. For example, monitoring wells provide little information on contaminant distribution in low-*k* zones, or natural assimilation processes that may affect contaminant longevity. From this CSM, characterizing the contaminant mass distribution in low-*k* soil zones, and identifying reactions that may be occurring in the low-*k* zones, are potentially key contributions to an updated CSM.

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5.0 TEST DESIGN

This section presents a detailed description of the activities that were conducted to address the performance objectives (Section 3.0) for the remediation performance evaluation at Site 17. In accordance with ESTCP guidance, this section includes (a) conceptual experimental design, (b) baseline characterization activities, (c) treatability and laboratory study results, (d) layout and design of technology components, (e) field testing, (f) sampling methods, and (g) sampling results.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

This project was designed to assess long-term remediation performance implementation of ZVI-Clay Soil Mixing. After implementation of soil mixing, the source-zone geology is transformed into a homogeneous body with ZVI and bentonite distributed throughout. As discussed in Section 4.0, the source area at Site 17 was likely to have contained TCE DNAPL prior to remediation, but post-remediation groundwater data suggests that TCE concentrations had been reduced to levels at or near MCLs. The source-zone remediation was highly effective in reducing contaminant concentrations, but following the CSM (Section 4.4), uncertainties remain regarding (a) fate of the relatively small amount of contaminant mass remaining in the treated source zone, (b) impacts of the source-zone remediation downgradient of the treated zone, and (c) contaminant mass distribution and processes in low-*k* zones.

To address these uncertainties, the conceptual experimental design consisted of collecting high-resolution data from locations within and downgradient of the mixed-soil zone, using the C_3 technology as developed under ER-1740. The testing was also designed to provide high-resolution data that could be compared to existing remediation performance data. Thus, the soil-core sample locations were generally selected to align with nearby monitoring wells for ease of comparison. The target depth intervals for core collection were selected based on existing knowledge of site geology (described in Section 4.2) and contaminant distribution (Section 4.3). The C_3 data are intended to supplement existing soil and groundwater data with high-resolution data, representing the underlying low-*k* aquitard as well as transmissive zones. Specific soil-core locations and sampling depth intervals are described in Section 5.4. The general procedures used for collection, processing, and analysis of frozen cores were based on the protocols established under ER-1740 (Sale et al. 2016); refinements to these protocols were implemented to address the project-specific performance objectives, defined in Section 3.0.

5.2 BASELINE CHARACTERIZATION ACTIVITIES

This work involved a single sample collection event, completed in June 2016, followed by extensive characterization and analyses. In support of this work, baseline characterization consisted of evaluating existing remediation performance monitoring data that has previously been collected (i.e., no "baseline" data collection was conducted as part of this work). The Soil Mixing Completion Report (CH2M HILL 2013), Site 17 Year 2 Post-Soil-Mixing Monitoring Report (CH2M HILL 2015), and additional data provided by CH2M HILL, were referenced for baseline data. Baseline data included in the evaluation consisted of water levels, concentrations of TCE and related degradation products (*c*DCE, VC, ethylene, ethane), concentrations of inorganic species, and various other geochemical parameters.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

No treatability testing was conducted as part of this work.

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The ZVI-Clay Soil Mixing remediation technology is described in Section 4.0, and a detailed description of implementation at Site 17 was produced by CH2M HILL (2013). The layout of technology components utilized for high-resolution characterization at Site 17 (i.e., coring locations) is based on the mixed-soil zone boundaries and other site features, including existing monitoring wells and Mattawoman Creek. This subsection includes a description of the equipment used and sampling locations for cryogenic coring activities conducted at Site 17. Photographic documentation of the cryogenic coring procedures is provided in Appendix E.

5.4.1 Equipment Description

The C_3 procedures and sampling equipment were based on those developed under ER-1740 for ER-1740 (Sale et al. 2016 and Kiaalhosseini et al. 2016). Both of these references describe two systems for LN circulation: a coiled-tubing system and a dual-wall chamber system; the dual-wall chamber system was utilized for this project. A brief description of the C_3 equipment, and modifications to the system developed under ER-1740, is presented herein.

Cryogenic coring was completed using a modified 4¼-inch ID hollow-stem auger system (Figure 15) and 4-inch OD continuous sample system (Figure 16; described in Section 2.1). The modified continuous core-barrel sampler was designed by CSU, OHSU, and DEI; development was funded by the SERDP (ER-1740), Colorado Office of Economic Development and International Trade, Chevron, ExxonMobile, and Chemours. The modified system is designed to collect a 30-inch long soil core in a 2½-inch OD core liner. The interstitial space accommodates the LN circulation system and a layer of ¼-inch closed cell foam insulation (Figure 17). The drive shoe (Figure 17) is modified to securely seat a 2 ½ -inch core liner in a 4-inch continuous sample barrel.

Ultimately, the purpose of the modified core-collection system is to freeze soil cores *in situ*, via circulation of LN. Components of the LN circulation system are shown in Figure 18. The core-barrel drive head is drilled to allow for inlet and outlet LN lines. The inlet LN port is connected to a pressurized dewar, via an insulated line, and the outlet LN port is connect to a back-pressure control device. Back-pressure is applied to control the rate of LN volatilization; by ensuring that substantial LN remains in the liquid phase until reaching the sample, the cooling capacity of LN can be optimized. The back-pressure device is also equipped with instrumentation, including pressure and temperature gauges, to monitor status of freezing. Additional details are provided below.

Figure 15. Photos of Hollow Stem Auger Rig and Support Vehicle Used for Cryogenic Coring.

The hollow stem auger rig is owned and operated by DEI, and the support vehicle (Penske moving van) was rented for this project.

Figure 16. Core-barrel Sampler Photos.

See Kiaalhosseini et al. (2016) for a thorough description, including schematic illustration.

Figure 17. Photos of Core Barrel Sampler.

(Left) Removal of core-barrel drive shoe and (right) end view of modified continuous core-sample barrel.

Figure 18. Photos of LN circulation.

(Upper left) LN dewar, (upper right) LN inlet and outlet ports, (lower left) LN backpressure control device, and (lower right) LN exhaust plume during LN circulation.

5.4.2 Soil-Core Collection Locations

The soil-core collection locations are shown in Figure 19, and additional information on the locations is provided in Table 4. The locations were selected based on the performance objectives for this work. Two locations were selected from within the former source area: (a) a former high-concentration zone, which was presumed to contain TCE DNAPL based on pre-remediation concentration data, and was in the treated-zone area that was admixed with excess ZVI (>3%), and (b) a treated-zone location that initially contained lesser concentrations (<1 mg/L), and was mixed with a target amount of 1% ZVI. Four locations were selected outside of the treated zone to evaluate impacts of source-zone remediation. The locations outside of the treated zone (i.e., "downgradient" locations) were selected to create transect lines in two directions, which have historically been impacted by contaminants, but may be subsequently influenced by source-zone remediation.

The transect lines are indicated on Figure 19. Where possible, soil-core locations were selected to be near existing monitoring wells, to facilitate a comparison to existing data.

Table 4. Soil-Core Location Summary

Soil-Core Location	Sample Collection Date/Time	Description	Nearby Monitoring Well	Sampled Depth Interval (ft bgs)	Notes
IH17SA1*	6/21/2016 08:15	Source area, low concentration	MW07	2 to 22.0	
IH17SA2*	6/21/2016 12:30	Source area, high concentration	MW08	2 to 19.5	
IH17DG1A*	6/23/2016 08:30	Downgradient Transect DG1, near source	-	7 to 19.5	Sample collection started at 7 ft due to buried wood
IH17DG1B*	6/23/2016 11:30	Downgradient Transect DG1, distal to source	MW10	7 to 19.5	Sample collection started at 7 ft due to buried wood
IH17DG2A*	6/22/2016 13:25	Downgradient Transect DG2, near source	-	2 to 19.5	Lower location moved due to obstacle encountered
IH17DG2B*	6/22/2016 08:00	Downgradient Transect DG2, distal to source	MW02	2 to 19.5	Lower location moved due to obstacle encountered

Notes:
***The cryogenic coring locations are herein referred to by their abbreviated names, with "IH17" excluded.**

At all of the soil-core locations outside of the mixed zone, buried wood was encountered at about 5 to 7 ft bgs. From conversations with site personnel, the historical ground surface was at this level, and tidally-deposited wood was subsequently buried to a depth of about 5 to 7 feet. The buried wood is noted in the soil-mixing report (CH2M HILL 2013), and was excavated from the remediated zone prior to soil mixing activities.

During the field sampling activities, the buried wood affected the core collection by causing refusal, or blocking soils from entering the core barrel. For each of the four downgradient locations, the obstructions encountered, and method of handling the obstruction were as follows (in chronological order):

- DG2B: a solid obstruction was encountered at about 5.5 ft, causing refusal. This was resolved by moving about 3 feet toward monitoring well MW02, auguring a depth of 4.5 ft, and resuming cryogenic coring.
- DG2A: a layer of wood was encountered at about 7 ft bgs; the wood appeared to block soil from entering to core barrel at greater depths. This was resolved by moving about 3 feet toward monitoring well MW02, auguring to a depth of 8 ft, and resuming cryogenic coring.
- DG1A: an investigative boring was augured and wood was discovered at 5 to 5.5 ft; cryogenic coring was started at 7 feet bgs.
- DG1B: an investigative boring was augured and wood was discovered at 5 to 5.5 ft; cryogenic coring was started at 7 feet bgs.

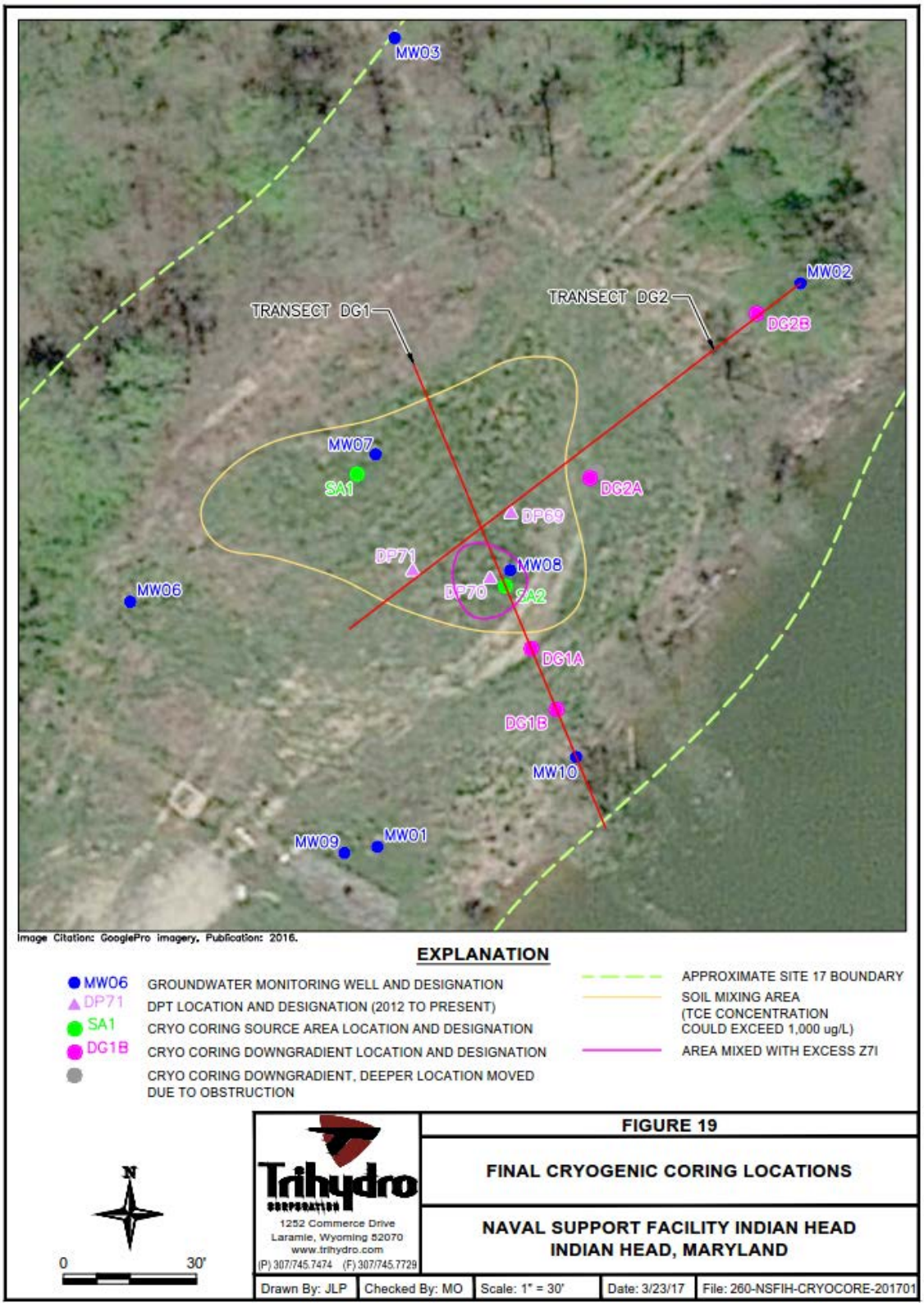

Figure 19. Final Cryogenic Coring Locations.

5.5 FIELD TESTING

This project consisted of field sample collection, using cryogenic coring, and subsequent high-resolution characterization. Field sample collection was completed between June 20 and 24, 2016. Following field work, samples were sent to CSU for analysis. The subsequent processing and sample analysis work was largely completed during the two months following field sampling (July and August, 2016). Following frozen-core processing and analysis, a detailed comparison between C_3 data and existing remediation performance assessment data was performed. The schedule for field work, sample processing, and subsequent analysis is shown in a Gantt chart (Figure 20). Details regarding specific phases of the field testing are provided below.

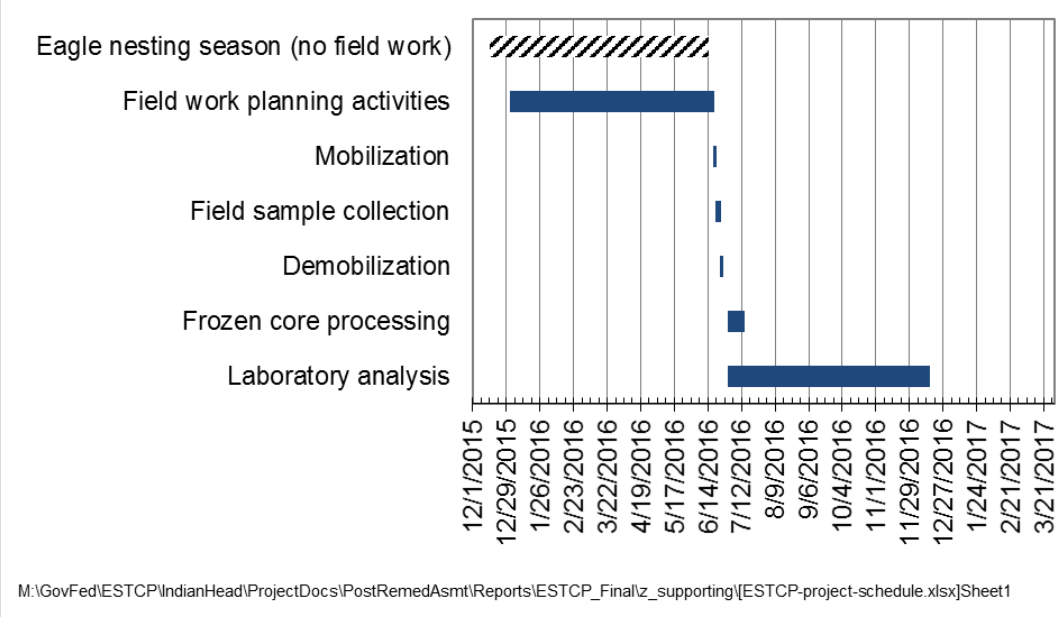

Figure 20. Completion Schedule for Field and Laboratory Activities.

Field work was not allowed to commence at Site 17 until June 15, 2016, due to nesting bald eagles. Field work was therefore conducted during the first full week after the site was cleared for construction. Mobilization consisted of transporting drilling equipment and personnel to the site. DEI conducted the drilling, using drilling equipment mobilized from Fort Collins, CO (at this time, the DEI cryogenic coring tool is the only commercially available C_3 tool). Personnel from Trihydro were on site for the drilling activities to provide oversight, handle frozen core samples once collected at the surface, and contribute to decisions. Dr. Rick Johnson (OHSU) was also on site to provide consulting services during the drilling activities.

Field sample collection started with a site safety orientation, review of the Accident Prevention Plan (APP) and Trihydro Health and Safety Plan (HASP), and tailgate safety discussion. For sample collection, core was collected from two locations per day. Thus, collection of core from six locations required three days of actual core collection, plus one day each for mobilization and demobilization (cleanup). Tailgate safety meetings were held daily, in accordance with the APP/ HASP. Clearance for unexploded ordinance (UXO) was conducted by CH2M HILL for the four sample locations outside of the mixed-soil zone (the mixed soil zone was cleared in 2012, prior to remediation activities).

Demobilization consisted of cleaning up the work area and decontamination. This work resulted in open boreholes and generation of Investigation Derived Waste (IDW). The boreholes were abandoned via backfilling with bentonite, and in accordance with site-specific requirements. Aside from the backfilled boreholes, additional site impacts were limited (i.e., no monitoring wells or other infrastructure were left in place). In addition, IDW included cuttings and contact-contaminated materials. Uncontaminated waste was scattered at the site, per instruction from site personnel. Equipment decontamination consisted of steam washing.

Processing was completed at the CSU laboratory from July 5 to 13, 2016. Most of the sample analysis was completed over the subsequent six months (Section 5.6.2). Remediation performance assessment, which consisted of data analysis and comparison to existing soil and groundwater data, was completed as cryogenic coring data became available (Section 6.0).

5.6 SAMPLING METHODS

The primary purpose of this work was to assess the long-term impacts of source-zone remediation; high-resolution soil core data provided the means to enhance the value of this assessment. Due to the need for high-resolution data, and to enhance the likelihood of preservation of sensitive parameters (e.g., volatile constituents and microbial community), the soil cores were collected using the C_3 technology. Soil coring locations were selected to meet the project-specific performance objectives, which included assessing geochemical conditions within and downgradient of the treated source zone. Specific procedures used for C_3 activities and subsequent processing of frozen core are presented in this section.

At each location, the surface soils were augured until the target starting depth for cryogenic coring was reached. The target depth was 7 ft for two locations (DG1A and DG1B), due to buried wood, and 2 ft for all other locations (Table 4). Next, the continuous core-sample barrel was fitted with a core liner (30-in.-long × 2 ½-in. OD, constructed of transparent PVC. The sample barrel was then advanced to the target depth using the hollow-stem auger rig. Once at depth, the LN system was connected. LN was circulated for approximately 6 minutes to freeze the sample. Pressure and temperature data were recorded during LN circulation to evaluate the freezing time. The LN system was then disconnected and the core barrel removed from the ground. The liner, containing frozen soil core, was then removed from the core barrel (Figure 21).

Upon recovery at the surface, each core segment was inspected and notes were recorded including location, depth, sample time, recovery, and geology. The core was then labeled, wrapped in bubble wrap, and placed in a cooler on dry ice. Core sections were individually wrapped in bubble wrap to minimize risk of breakage of the liner, which may become brittle when frozen.

Figure 21. Photos of Frozen Core Removal from the Continuous Sampler.

(Left) Removal of the frozen core liner from the continuous sample barrel and (right) handling a frozen core after removal.

Core samples were stored and shipped in Rubbermaid 150-qt. Marine coolers. Sample coolers were shipped from Waldorf, MD to Fort Collins, CO via FedEx for next-day delivery. About 50 lb. of dry ice (purchased from Circus Ice Cream, Waldorf, MD) were included with each cooler at the time of shipment. In total, the project required purchase of three 150-qt coolers and 192 lb. of dry ice. Upon receipt at CSU, the frozen cores were stored in a cryogenic freezer at -80°C. Processing and analysis was conducted in a laboratory at CSU.

Processing of the frozen cores was conducted by CSU and generally followed the protocol established under ER-1740 (Sale et al. 2016), with minor exceptions as noted. For sampling, the soil cores were cut into 1-inch thick frozen-sample discs ("hockey pucks") at an approximate rate of one sample per 6 inches of frozen core, and the "hockey pucks" were then quartered (illustrated in Figure 22) for subsequent analyses. At select locations, subsamples were collected at a higher frequency for duplicate or high-resolution analysis.

The procedure of cutting frozen core into subsamples is shown in Figure 23 through Figure 25. A jig was used to measure a 1-inch section of core, and the subsample was then cut using a cut-off saw (Hitachi) equipped with a 14-in. diameter "Metal Cut-Off" blade (Diablo). Photographs of the frozen-core cutting procedure are shown in Figure 23. Next, the frozen core was divided into subsamples for subsequent analyses (Figure 24). The frozen core cutting, subsampling, and extractions were conducted using an assembly-line approach (Figure 25) to ensure that extractions were completed before the soil thaws.

As discussed previously, the frozen core discs were quartered (while frozen) for subsequent analysis. The typical analyses conducted on the four sample quarters are illustrated in Figure 22. In addition, the 5-in. sections of frozen core between the "hockey pucks" were analyzed for properties including hydraulic conductivity. Select intermediate samples were also tested for reactivity toward TCE.

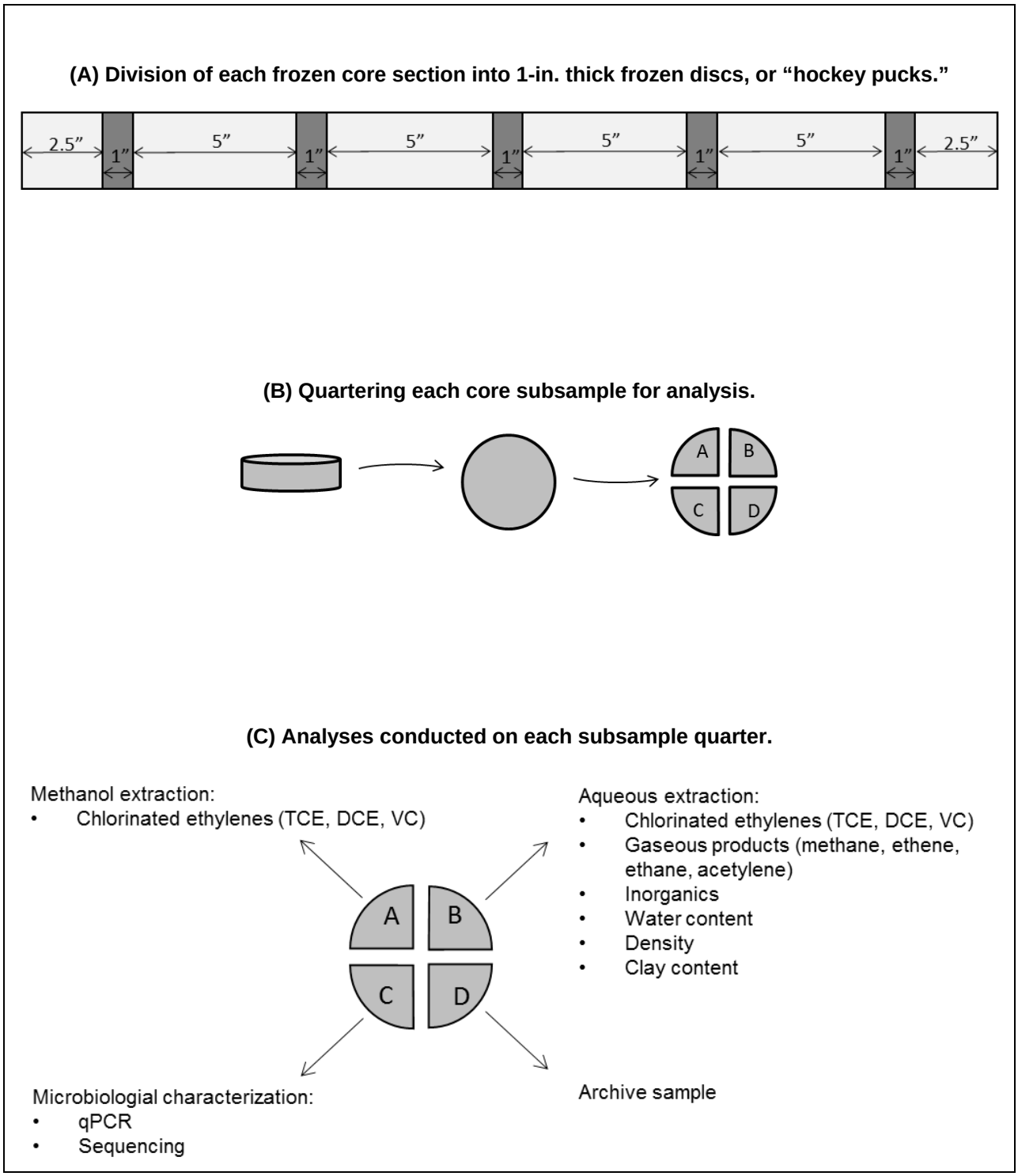

Figure 22. Road Map for Frozen Core Analysis.

Figure 23. Photos of Cutting of Frozen Core into "Hockey Pucks."

(Left) measuring 1-inch core sections using a jig, (center) cutting of a core in progress, and (right) after cutting is complete.

Figure 24. Generating Subsamples and Handling of Subsamples in Preparation for Extraction.

(Left) CSU Undergraduate student Tyler Cloud, dividing core subsample into quarters, (right) handling of quartered subsamples in preparation for extraction.

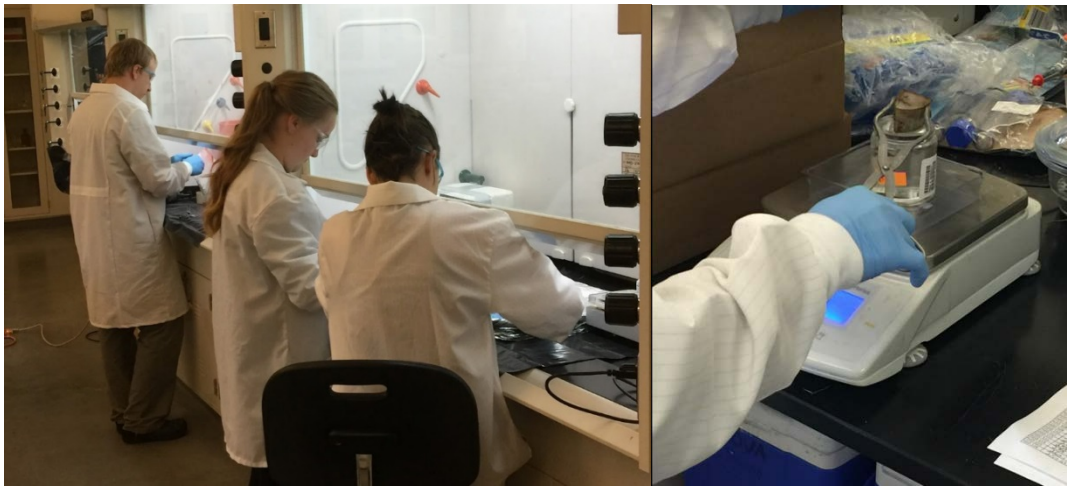

Figure 25. Processing of Subsamples after Quartering.

(Left) CSU undergraduate students, including (from left to right) Tyler Cloud, Christina Ankrom, and Anna Hoyt and (right) processing core after quartering and aqueous extraction of a subsample.

A summary of number and types of subsamples is shown in Table 5. A similar suite of analyses was conducted on soil cores collected within and outside of the mixed-soil zone. All core subsamples were analyzed for chlorinated ethylenes (PCE, TCE, DCE isomers, and VC), gaseous products (methane, ethane, ethylene, and acetylene), dissolved-phase anions, and dissolved iron (total and Fe^{2+}). Primarily mixed-zone cores were analyzed for ZVI content and reactivity. Select subsamples from both treated-zone and downgradient cores were analyzed for microbial characterization and soil properties. Analytical methods employed for these analyses are summarized in Table 6, and described in detail in the following subsections. Additional sampling information, including Quality Assurance sampling, decontamination procedures, and sample documentation, is provided in Appendix F.

Table 5. Total Number and Types of Samples Collected

Component	Matrix	Number of Samples	Analyte	Location
Mixed-soil zone core	Soil	2 cores, approximately 40 samples	• TCE, PCE • DCE isomers, VC • Methane, ethane, ethylene • Dissolved anions • Dissolved iron	One sample per foot of core
		1 per core	Complete VOCs	Near center of core
		3 per core	Soil properties	Top, middle, and bottom of core
		8-10 per core	ZVI content and reactivity	1 sample per 2 feet of core
		3 per core	Microbial counts	Top, middle, and bottom
		1 per core	Microbial characterization	Near center of core
		1 per core	Reduction potential	Near center of core
Downgradient soil core	Soil	3 cores, approximately 60 samples	• TCE, PCE • DCE isomers, VC • Methane, ethane, ethylene • Dissolved anions • Dissolved iron	One sample per foot of core; additional samples collected at zones of geologic interest
		1 per core	Complete VOCs	Near center of core
		3 per core	Soil properties	Top, middle, and bottom
		3 per core	Microbial counts	Top, middle, and bottom
		1 per core	Microbial characterization	Near center of core
		1 per core	Reduction potential	Near center of core

Table 6. Analytical Methods for Sample Analysis

Matrix	Analyte	Method	Container	Preservative	Holding Time
Soil	TCE and PCE	GC/ECD[1]	120-mL jar/ MeOH ext.	None	28 days[7]
	DCE isomers and VC	GC/MS[2]	120-mL jar/ MeOH ext.	None	28 days
	Methane, ethane, and ethylene	GC/FID[3]	20-mL Headspace	None	48 hours
	Dissolved anions	IC[4]	120-mL jar/ water ext.	None	28 days
	Dissolved iron: Fe^{2+} and total Fe	Colormetric/ Spectrophotometry	120-mL jar/ water ext.	None	14 days
	Complete VOCs	EPA 8260	40-mL VOA	None	28 days[7]
	Microbial counts	qPCR[5]	-80°C[8]	None	56 days
	Microbial characterization	DNA ext. & sequencing	-80°C[8]	None	56 days
	RNA characterization (experimental)	RNA ext. & sequencing	-80°C[8]	None	28 days
	Hydraulic conductivity	Sale et al. 2015	Measured in liner	None	28 days
	ZVI	Magnetic separation	Custom[6]	None	28 days
	Redox	ER-2308	Custom[6]	None	28 days

Notes:
1 – Gas Chromatograph / Electron Capture Detector
2 – Gas Chromatograph / Mass Spectrometric Detector
3 – Gas Chromatograph / Flame Ionization Detector

4 – Ion Chromatograph
5 – Quantitative Polymerase Chain Reaction
6 – Container to be customized for specialty analyses
7 – Holding time after methanol extraction
8 – Soils will be tightly wrapped in sterile aluminum foil and placed in a freezer at -80°C

5.6.1 Methanol Extraction

Methanol-extract vials were analyzed for VOCs, including TCE, *c*DCE, *trans*-1,2-dichloroethylene (*t*DCE), and VC. For this extraction, 30 mL of High Performance Liquid Chromatography (HPLC)-grade methanol was added to 125-mL glass jars with polytetrafluoroethylene (PTFE)-lined caps. The weight of each jar with methanol was recorded. For each sample, one of the sample quarters was added to the extraction jar immediately after processing (i.e., while still frozen). The cap was then sealed and the extraction-jar weight, with sample, was recorded. The methanol-extraction jars were placed on a vortex mixer for 10 minutes followed by an ultrasonication bath for 30 minutes. The jars were stored in a refrigerator (approximately 4°C) until analysis.

Analysis of the methanol extract was conducted on an Agilent 6890 gas chromatograph (GC) equipped with an Agilent 5973 mass spectrometric detector (MSD). The methanol extract was directly injected into the GC using an autosampler. The method utilized a Restek Rxi-624Sil MS column, with the following dimensions: 30-m length, 0.25-mm OD, and 1.4-µm film thickness. The MS detector was operated in single ion mode (SIM). A set of at least five calibration standards, with concentrations spanning the range of reported concentrations, were injected with each batch of analyses.

Calibration standards for chlorinated ethylenes involved preparation of a stock solution in high-purity (>99.5%) methanol. Standards for TCE and DCE isomers were prepared via dilution of the neat chemicals (>99% for TCE and *c*DCE; >98% for *t*DCE) in high-purity methanol. VC was added to the calibration standards via a stock solution (purchased from Ultra Scientific) of 2000 mg/L in methanol. Samples were diluted to target concentrations and then transferred into GC vials for analysis. At least five calibration standards were included, with a range spanning reported values.

5.6.2 Aqueous Extraction

Aqueous-extraction vials were analyzed for organics (chlorinated ethylenes and gaseous products), inorganics (anions and dissolved iron), and physical properties. Procedures employed for each of these analyses are described below.

Prior to sample processing, the aqueous extraction jars were prepared by filling each jar with de-aired de-ionized (DADI) water; the water was deionized to 18.3 MΩ and subsequently de-aired by placing under vacuum (approximately 630 mm Hg) for at least 30 minutes. Aqueous-extraction jars were filled with DADI water to the top, such that there was no headspace, in an anaerobic chamber. The lids were then emplaced, sealing the jars with (ideally) no headspace. The jars were stored in the anaerobic chamber until approximately one day before sample processing.

At the time of processing, the following procedures were implemented for each sample. Immediately prior to extraction of each sample, a plastic dish was placed on a scale, which was then tared; the aqueous extraction jar was then placed in the dish, and the weight (jar plus DADI water) was recorded. Next, as the sample was processed, a series of steps were completed in rapid succession: (1) immediately after quartering of the sample, the lid was removed from the aqueous-extraction jar; (2) one of the sample quarters was placed in the jar, which displaces water from the jar into the plastic dish; and (3) the lid was re-placed, sealing the jar (now with sample) with no headspace. After these steps were complete, the weight was recorded to determine the sample mass. The extraction jar was then removed from the dish, and the weight of displaced water was recorded; this weight was converted to a volume of displaced water to determine the sample density. Samples were then placed on a vortex shaker for approximately 10 minutes to disperse solids and facilitate extraction prior to analysis. The aqueous extract was analyzed for VOCs and gaseous products within 48 hours of sample collection. The jars were stored in a refrigerator (approximately 4°C) until subsequent analysis for inorganics and physical properties.

Organics Analysis. Analysis of the aqueous extract for VOCs and gaseous products was conducted on an Agilent 6890 GC equipped with a flame ionization detector (GC/FID). For this analysis, 5 mL of the aqueous extract was transferred into a 20 mL headspace vial, which was then crimp-sealed using a PTFE-lined septa cap. Samples were injected into the GC using a Tekmar 7000 headspace autosampler, following a 5-minute equilibration period at 40°C. The method utilized a Restek Rt-Q-BOND column, with the following dimensions: 30-m length, 0.32-mm OD, and 10-µm film thickness. Analysis was conducted for TCE, *c*DCE, *t*DCE, VC, ethane, ethylene, acetylene, and methane in a single injection.

Calibration standards for chlorinated ethylenes involved preparation of a spiking solution in high-purity (>99.5%) methanol. Standards for TCE and DCE isomers were prepared via dilution of the neat chemicals (>99% for TCE and *c*DCE; >98% for *t*DCE) in high-purity methanol; VC was added to the calibration standards via a stock solution (purchased from Ultra Scientific) of 2000 mg/L in methanol. The spiking solutions were added to 5 mL of deionized water (DIW) in the headspace vials. Calibration standards for methane, ethane, ethylene, and acetylene were prepared using a Scotty® (Air Liquide) calibration gas standard containing 4380 ppm of each analyte. For the gaseous analytes, headspace vials were prepared with 5 mL of DIW and then sealed; varying volumes (ranging from 10 to 500 µL) of the stock solution were injected into the headspace vials through the septa, using glass gas-tight syringes. Calibration standards for the chlorinated ethylenes and gaseous products were analyzed via GC/FID using the same headspace injection and analytical methods as described above for the aqueous-extract samples.

Inorganics Analysis. Analysis for inorganic analytes, including dissolved iron and anions (chloride, nitrate, and sulfate) was completed after gaseous analysis was complete. Approximately half of the aqueous extraction vials were analyzed for inorganics. For inorganics, an aliquot of aqueous extract was collected from select extraction vials using a disposable 10-mL plastic syringe. The solution was filtered through a 0.45-µm syringe filter. Samples of the filtered solution were analyzed for anions using a Dionex (IP25) ion chromatograph (IC) equipped with a Dionex AS14A column.

For dissolved iron analysis, methods were based on those presented by Sale et al. 2015. Briefly, colormetric methods were employed, using Hach (Loveland, CO) reagent kits for ferrous iron and total iron (Ferro-Ver). A stock solution was prepared with the Hach reagents in DIW. The Hach-reagent stock solution was added to a 2.0-mL cuvette, along with an aliquot of the filtered extract solution, in quantities such that the measured water and reagent were mixed in the cuvette in the proper quantities. Analysis was conducted using a Thermo Scientific Genesys 10uv spectrophotometer. Calibration standards were prepared via dilution in DIW of a 100 mg/L total-iron solution (Hach).

Properties Analysis. The aqueous-extraction sample jars were used to evaluate physical properties of the soil samples. The properties evaluation include bulk density (wet sample basis) and clay content.

The wet bulk density, ρ_b (gm/cm^3), was calculated based on weights recorded during extraction. The sample mass was calculated as the difference between weight recorded before and after sample addition. The volume of the sample was calculated by the volume of water collected in the plastic dish. The value of ρ_b was then calculated as the sample mass divided by volume of water displaced (assuming an aqueous density of 1.0 gm/cm^3).

The clay content was estimated using a novel procedure that was devised as part of this project. The semi-quantitative procedure resulted in calculation of a "Clay Content Index," or a value that represents the relative amount of clay in each sample. The clay content index is established based on the settlement rate of solids in each sample. To calculate the Clay Content Index, each vial was hand mixed at the beginning of the test, and then kept relatively stationary (at approximately 4°C) for the remainder of the test. Each vial was then inspected after settlement times of 1, 3, and 8 days (these times were selected based on casual observation of settlement within the vials; differential settlement rates became apparent after these times). With each inspection, the vial was assigned a rating value of 0 to 3 based on the observed clarity of the solution. The ratings were assigned as described below. The reported Clay Content Index value was the average of the suspended-solid ratings observed at each of the three times.

Rating = 0: No visible suspended solids; solution was clear or minor colored tint apparent due to dissolved species.

Rating = 1: Minor amounts of suspended solids were present; light passed through the entire sample, but solution did not appear to be clear.

Rating = 2: Substantial suspended solids present; light partially passed through solution but the observer could not see through entire sample.

Rating = 3: High levels of suspended solids made solution opaque; light did not pass through the solution for any noticeable distance.

5.6.3 Microbiological Characterization

Although microbiological characterization was not one of the core analyses conducted in this project, analysis was conducted to supplement geochemical data. Microbiological community preservation presents a potential key advantage to collecting cores cryogenically. At this stage in development, the techniques for microbial extraction and analyses are considered to be works in progress.

Microbiological characterization was conducted using one of the sample quarters generated during processing. Immediately after cutting the core into a frozen disk and quartering, one of the sample quarters was wrapped in aluminum foil and returned to the freezer (-80°C) until DNA extraction. Microbial analysis was performed in triplicate following procedures similar to those described by Irianni-Renno et al. (2016). The samples were pretreated as described by Whitby and Lund (2009), with modifications, to remove potential contaminants (e.g., LNAPL), as described in Irianni-Renno et al. (2016). DNA was quantified via optical density at 260 nm with a Nanodrop™ 2000 reader (Thermoscientific, Wilmington, DE). DNA was extracted in triplicate from each sample and was subsequently stored at -20°C prior to quantitative polymerase chain reaction (qPCR) and next-generation sequencing analysis.

qPCR assays. SYBR™ Green (Life Technologies, Grand Island, NY) qPCR assays were used to quantify the bacterial and archaeal 16S rRNA genes. Genomic DNA extracted *from Desulfovibrio desulfuricans* (ATCC #:27774D-5) and *Methanosarcina acetivorans* (ATCC #: 35395D-5) was used to generate calibration curves for the bacterial and archaeal assays, respectively. The primer sets 27F / 388r and 931AF /1100Ar were used for amplification of bacterial and archaeal 16SrRNA genes, respectively. All assays were performed using an ABI 7300 real-time PCR system (Applied Biosystems, Foster City, CA). Each 25-µl SYBR™Green qPCR reaction included 1X Power SYBR™Green (Life technologies, Grand Island, NY), forward and reverse primers (2.5 µM), magnesium acetate (10 µM), PCR-grade water and 1 ng of DNA template. Thermocycling conditions were as follows: 95˚C for 10 min, followed by 40 cycles of 95˚C for 45 s, 56˚C for 30 s, and 60˚C for 30 s. Dissociation curve analysis was conducted to confirm amplicon specificity.

Next generation sequencing analysis. Sequencing analysis was performed by Research and Testing Laboratories, LLC (Lubbock, TX) using an Illumina MiSeq System (Illumina, San Diego, CA). Community profiling was performed targeting bacterial 16S rRNA genes with primers 28F and 519r and archaeal 16S rRNA genes with primers 517f and 909r.

Data analysis. Results from the microbial communities characterized were evaluated at multiple taxonomic levels. In this report, data are presented at three taxonomic levels (phylum, order and genus) for Bacteria and at two taxonomic levels (phylum and order) for Archaea (Appendix G).

Orders and genera that represent less than 3% of the community are combined with those that are unclassified, and reported as “other.” Phyla that represent less than 0.05% of the community are combined with those that are unclassified and reported as “other.” In addition, when analyzing the bacterial communities at the genus level, organisms that have been shown to share functional capabilities, such as sulfate reducers and methane oxidizers, were reported as groups (specific organisms in these groups are listed in Appendix G).

5.6.4 Archive

Archive samples were resealed immediately after processing, thus ensuring that they remained frozen. To reseal, the archive samples were wrapped in aluminum foil and vacuum-sealed in a polyethylene bag. The archive samples were immediately returned to a freezer, where they were stored at -20 °C. Select archive samples were analyzed for fraction organic carbon (f_{oc}) following methods described by Sale et al. 2015.

5.6.5 Hydraulic Conductivity Testing

Select intermediate samples were analyzed for hydraulic conductivity using the core-in-liner (CIL) method described by Sale at al. (2016). For the CIL method, end-caps were fabricated that seal the ends of the specimen within the core liner, thus allowing for hydraulic conductivity testing (in the vertical direction) without disrupting natural soil particle distribution. The CIL end caps are fabricated from acrylic, and Viton O-rings are used to provide a seal between the end-caps and the core liner. Stainless steel bolts are used to provide compression.

Hydraulic conductivity testing was conducted using a falling-head testing apparatus. The falling-head reservoirs consisted of 1.4-cm I.D. glass tubes, filled with de-aired tap water (City of Fort Collins); the tap water was de-aired by placing the water under approximately 630 mm Hg of vacuum for approximately 10 minutes. A photograph of the testing station is provided (Figure 26).

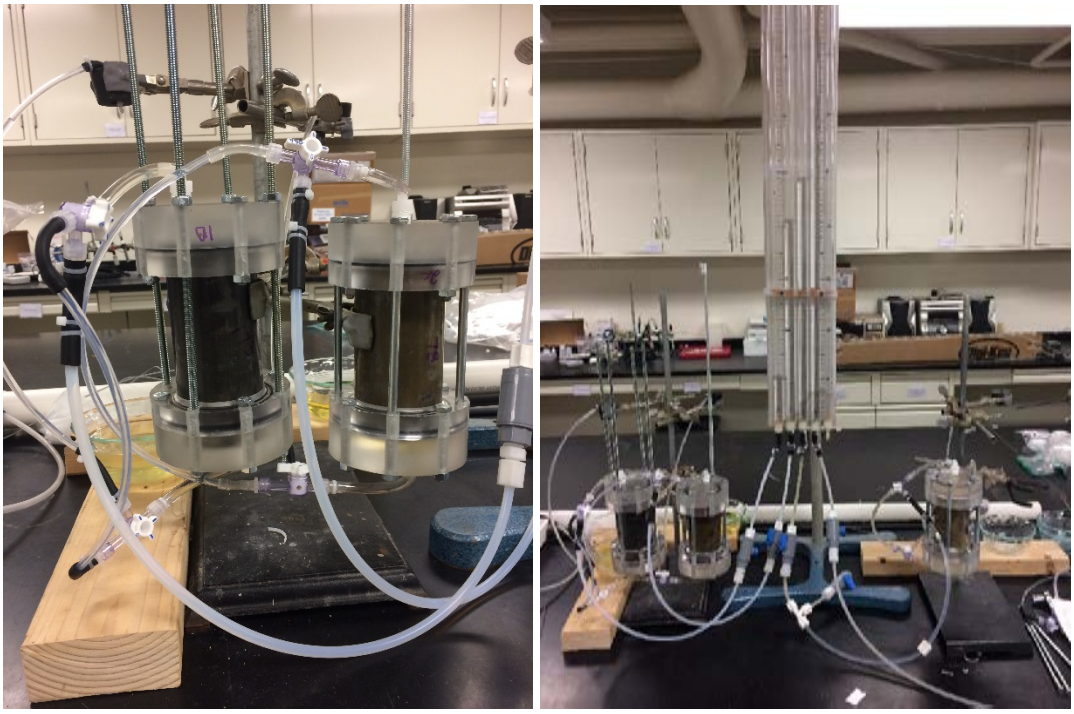

Figure 26. Photos of Hydraulic Conductivity Testing Apparatus.

(Left) CIL testing cells and (right) falling-head apparatus.

5.6.6 ZVI Content

ZVI content was analyzed in laboratory facilities at OHSU. The method employed involved acid digestion of the samples, followed by measurement of hydrogen production. Approximately 2.5 gm portions of frozen sample were transferred into pre-weighed 40-mL glass vials with septa caps. The sample vials were transferred into a glove box (atmosphere of <1.0 ppm oxygen with no hydrogen), where they were acidified using 10 mL of 1-molar hydrochloric acid. Samples were digested for 24 hours, during which they were vortex-mixed twice. After 24 hours of digestion, samples were analyzed for pressure and hydrogen content. First, pressure within each vial was measured through the septa. Second, samples were collected for hydrogen analysis.

For hydrogen analysis, 2-mL samples were collected in syringes, which were then transferred out of the glove box. Subsamples were injected into an SRI Instruments Model 8610C GC equipped with a Carboxen (ThermoFisher Scientific) 1010 PLOT column and a thermal conductivity detector. The GC temperature was isothermal at 30°C; nitrogen was used as a carrier gas. After analysis, the septa caps were opened to purge the headspace, the contents of each vial were mixed, and the vials were then re-sealed for another 24-hour digestion period. The 24-hr cycles of digestion/sampling/analysis were repeated for each sample until the produced hydrogen changed by less than 5%. Finally, vials were dried at 100°C for 24 hours to calculate water contents.

External calibration was conducted by preparing samples with known quantities of ZVI and analyzing the calibration samples using identical methods.

5.6.7 Reactivity Testing

Soil samples from six locations were analyzed for reactivity toward TCE. For reactivity testing, a 1-in. thick disc of frozen core was collected from each of the six soil-core locations, from sample depths of approximately 12 ft bgs. The core samples were thawed in an anaerobic chamber (atmosphere of nitrogen with approximately 1% hydrogen) and vented for approximately two weeks, to allow much of the volatile chlorinated compounds to escape. After this initial preparation, the sample specimens were analyzed for reactivity potential toward TCE.

The reactivity testing was conducted in 20-mL headspace vials, which were prepared in an anaerobic chamber. The study comprised 35 vials; each of the six samples were analyzed in replicates of five, and an additional set of control vials was prepared without soil. Each vial was prepared with 10 mL of DADI water; 5 gm (±1 gm) of the thawed sample; and 50 µL of a spiking solution, comprising TCE in methanol. The spiking solution was prepared by adding approximately 25µL of neat TCE (99%) to 4000 µL HPLC-grade methanol and then diluting in methanol to a concentration of approximately 1000 mg/L. The target post-spiking TCE concentration in the reactivity vials was 1 mg/L (in vials prepared with soil, the initial aqueous-phase TCE concentration was likely to be lower than the target level, due to sorption). Immediately after the spiking solution was added, the reactivity vials were crimp-sealed. The sealed vials were removed from the anaerobic chamber and placed on a vortex shaker for approximately 5 min to disperse solids. Until analysis, reactivity vials were placed in a controlled-temperature orbital shaker (Thermo Scientific MaxQ 6000) at 120 rpm and 19.0°C.

Reactivity vials were analyzed at reaction times of 1, 3, 7, 14, and 28 days. For each analysis event, one vial from each soil-core location, and a control vial, was removed from the orbital shaker for analysis. Vials were analyzed via GC/FID with headspace autosampler (as described in Section 5.6.2). The reaction vials were placed directly on the headspace autosampler and analyzed following the previously described methods, which were developed to provide concentraton data for TCE, DCE isomers, VC, ethylene, ethane, and acetylene. TCE concentrations are likely to be influenced by sorption. Thus, for the reactivity study, the data analysis focused on the degradation products as evidence of TCE degradation.

5.6.8 External Laboratory Analysis

Six samples of frozen soil, one from each soil-core location, were sent to an external laboratory for analysis. The objectives of external laboratory analysis included (a) comparing CSU analytical results to those generated by an external laboratory, and (b) identifying other organic compounds that may be present, aside from those included in this analysis. Methods are described in this subsection and results are presented in subsection 5.7.7.

The external laboratory samples consisted of archive samples, which were immediately returned to a freezer after packaging to maintain a frozen state. The samples were prepared for external analysis in December 2016, approximately five months after the original processing was complete. For preparation, six 40-mL glass vials were prepared with 5 mL of DIW and a magnetic stir bar, and weights recorded. Next, each sample was transferred from the freezer to a fume hood. While frozen, the sample was broken into smaller pieces (approximately 1 cm^3) using a stainless steel spatula. Pieces of the sample were added to the 40-mL vial until 5±1 g of frozen sample had been added. The vial was then sealed with a PTFE-lined septa cap. After preparation, the samples were hand delivered to ALS Laboratories (Fort Collins, Colorado) on the day of preparation. The six samples were analyzed by ALS following EPA 8260 protocol.

5.7 SAMPLING RESULTS

The primary data consists of high-resolution concentration data for chlorinated organic compounds (TCE, *c*DCE, and VC), gaseous organic compounds (acetylene, ethylene, ethane, and methane), inorganic anions (chloride, nitrate, sulfate), aqueous-phase iron (total and ferrous iron), and select soil properties (f_{oc}, density, clay content). Sampling results for each of these categories are tabulated in Appendix H; depth-discrete data is shown by location in Section 6.1 and cross section plots of select data are shown in Section 6.3. Select samples were also analyzed for ZVI content, total solid-phase iron, and biological analysis. Data are shown for organics, inorganics, and select soil properties. The measured methanol-extract concentrations were converted to a total-sample basis for presentation.

In the following results presentation, dashed lines are shown to indicate the approximate geologic transition between the underlying low-*k* clay aquitard and overlying zone. In source area ("SA") locations, the overlying zone comprises ZVI-Clay mixed soils, which were formerly heterogeneous with widely variable in terms of permeability, but have been homogenized and mixed with bentonite, and are now considered to be "low-*k*" (which was supported by results of hydraulic conductivity testing, Section 5.7.4). For the downgradient ("DG") locations, the overlying zone comprises interbedded sand/silt layers with depth-discrete variations in permeability.

The data described in this section for each analyte class (e.g., chlorinated organics, gaseous organics, inorganic species, and geology) are compared to the other analyte classes via parallel data plots in Section 6.1. The parallel data plots provide a detailed comparison of concentration data to geology and other soil properties.

5.7.1 Chlorinated Organics

Summary data are shown for the key organics, including TCE (Figure 27), *c*DCE (Figure 28), *t*DCE (Figure 29), and VC (Figure 30). Within each figure, results are shown for source-area soil-core locations (left); downgradient transect 1 (DG1), which includes two locations oriented toward MW10 (center); and downgradient transect 2 (DG2), which includes two locations oriented toward MW02 (right). Transects DG1 and DG2 are shown on Figure 19.

The data described in this section is compared to other data sets (e.g., gaseous organics, inorganic species, and geology) via parallel data plots in Section 6.1, and is presented in cross-section format in Section 6.3.

TCE concentrations range from non-detect (<0.01 mg/kg) to 0.3 mg/kg in the source-area samples; these concentrations are substantially reduced from pre-remediation concentrations, which were as high as 510 mg/kg. In source-area location SA1, TCE is noted in the clay beneath the mixed-soil interval (i.e., at a depth of greater than 18 ft bgs) at concentrations up to 0.5 mg/kg. In transect DG1, TCE is largely non-detect, with measureable concentrations (<0.3 mg/kg) occurring only in shallow samples (≤ 9 ft bgs). The greatest measured TCE concentrations occur in transect DG2 at depths of greater than 8 ft (DG2A) and greater that 13 ft (DG2B). The maximum measured TCE concentrations in DG2A and DG2B were 7300 and 75 mg/kg, respectively (note that the elevated concentration of 7300 mg/kg observed in DG2B appears to be an anomalous concentration spike occurring over a narrow depth interval; aside from this discrete sample, the highest measured TCE concentration in DG2B is 670 mg/kg).

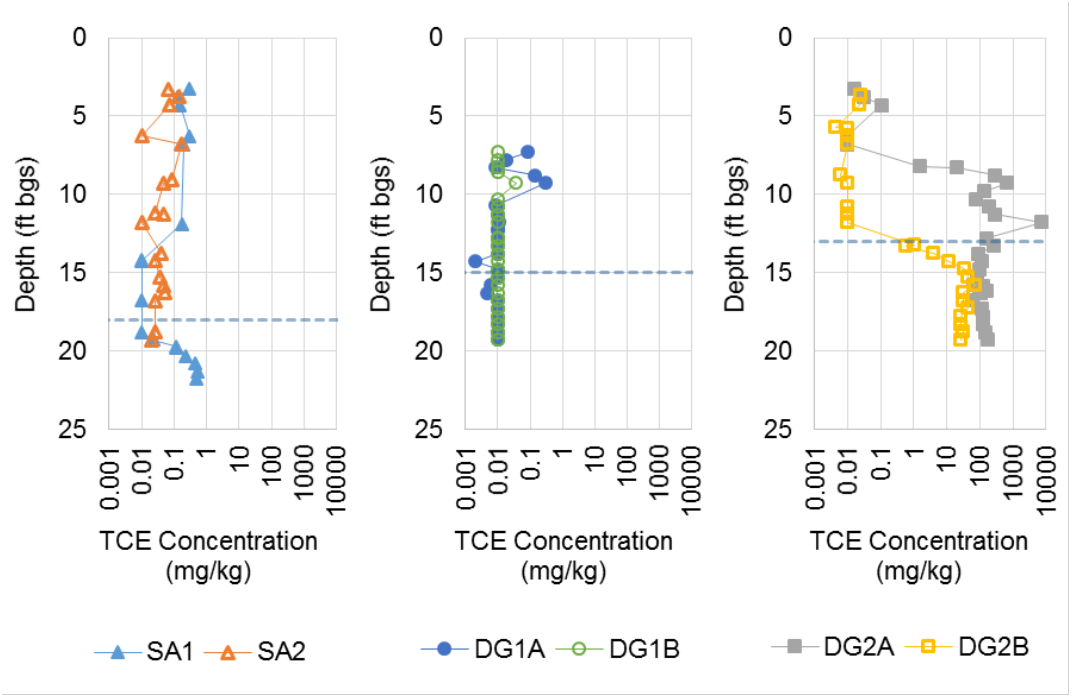

Figure 27. Concentration Data for TCE (methanol extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Concentrations of *c*DCE persist above detection limits (0.01 mg/kg) in samples collected from within the source-area, but only in shallower samples (i.e., depth less than 8 ft). Where detected, all *c*DCE concentrations were less than 0.85 mg/kg. In transect DG1, *c*DCE is largely non-detect, with measureable concentrations (up to 1.8 mg/kg) occurring only in shallower samples (<12 ft bgs). The highest measured *c*DCE concentrations occurred in transect DG2; the maximum *c*DCE concentrations in locations DG2A and DG2B were 170 and 8.3 mg/kg, respectively.

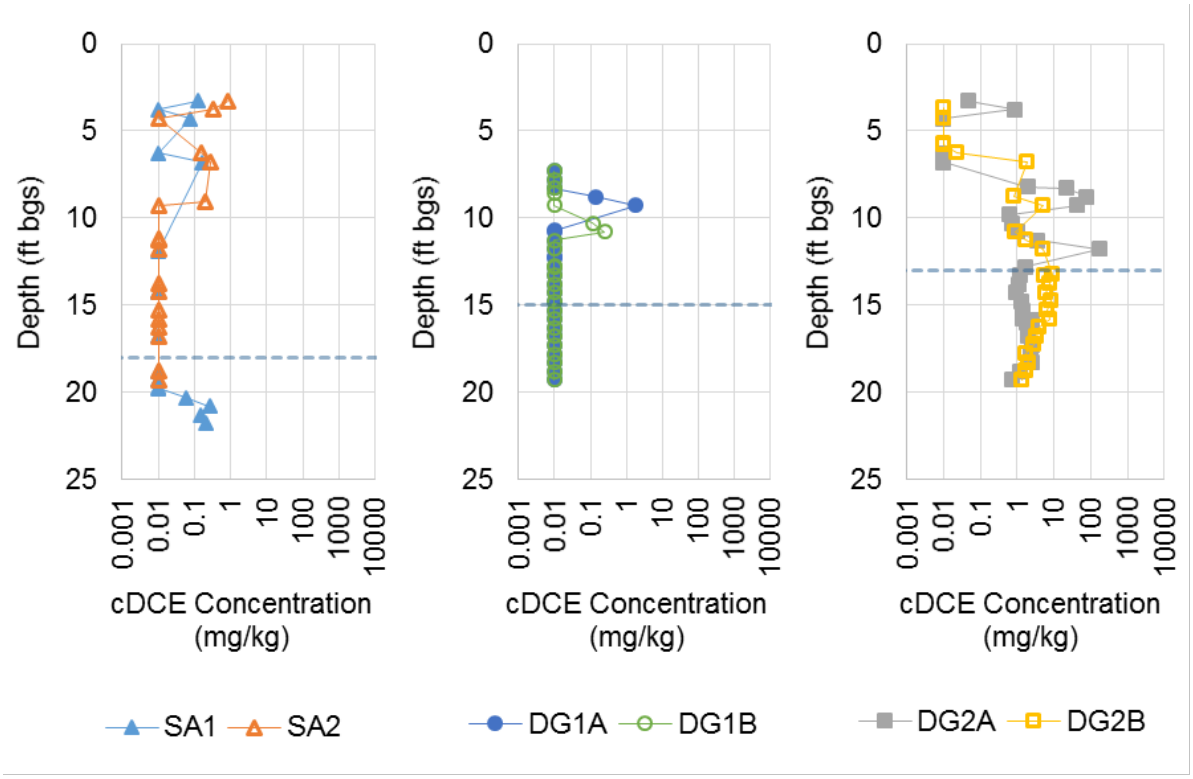

Figure 28. Concentration Data for *c*DCE (methanol extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Concentrations of *t*DCE were below detection limits (<0.01 mg/kg) in almost all samples collected from within the source-area. Similarly, in transect DG1, *t*DCE was not detected in any samples. Low levels of *t*DCE were detected in samples from DG2 over relatively narrow depth intervals, but *t*DCE was not detected in most samples. The maximum *t*DCE concentrations in locations DG2A and DG2B were 0.4 and 1.5 mg/kg, respectively.

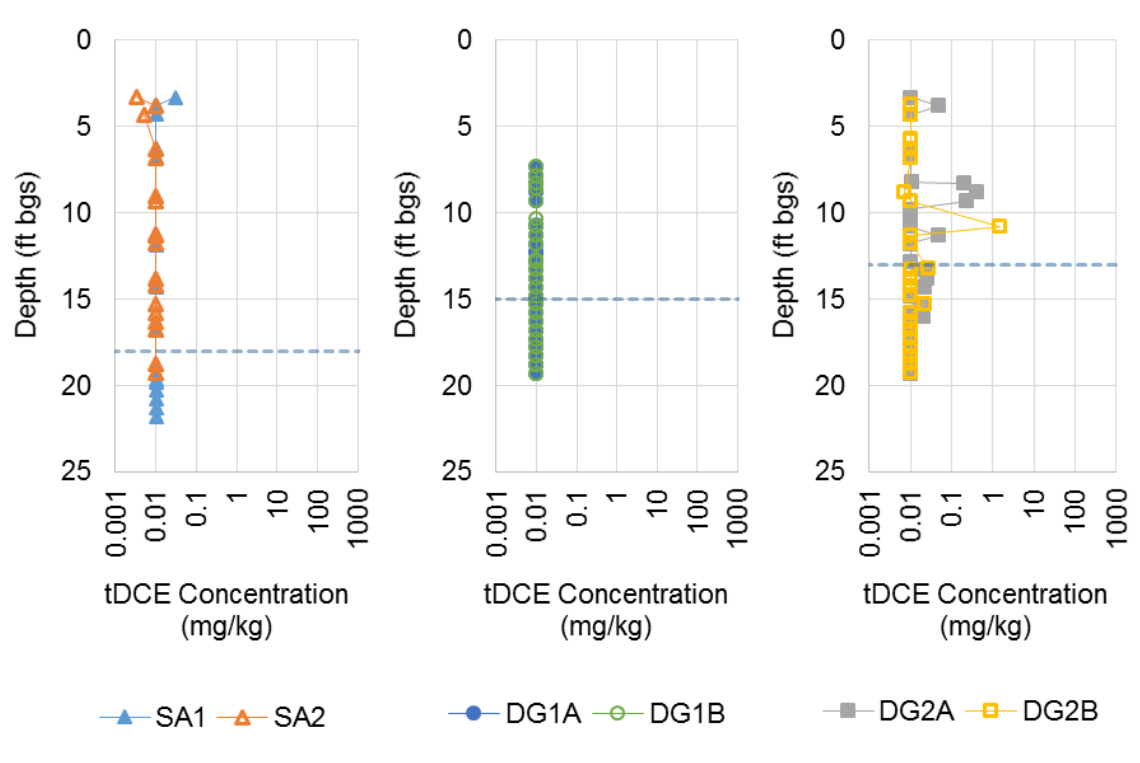

Figure 29. Concentration Data for *t*DCE (methanol extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

VC was below detection limits (0.01 mg/kg) in all source-area samples, with one exception (0.14 mg/kg). In transect DG1, VC was detected primarily in shallow samples (i.e., <13 ft bgs); the highest detected VC concentration in DG1A and DG1B were 7.5 and 1.4 mg/kg, respectively. VC was detected in several samples from transect DG2. In location, DG2A, VC was sporadically detected over the entire sampling interval, at concentrations up to 7.5 mg/kg. In location DG2B, VC was detected primarily in deeper samples (> 6 ft bgs), at concentrations up to 11 mg/kg.

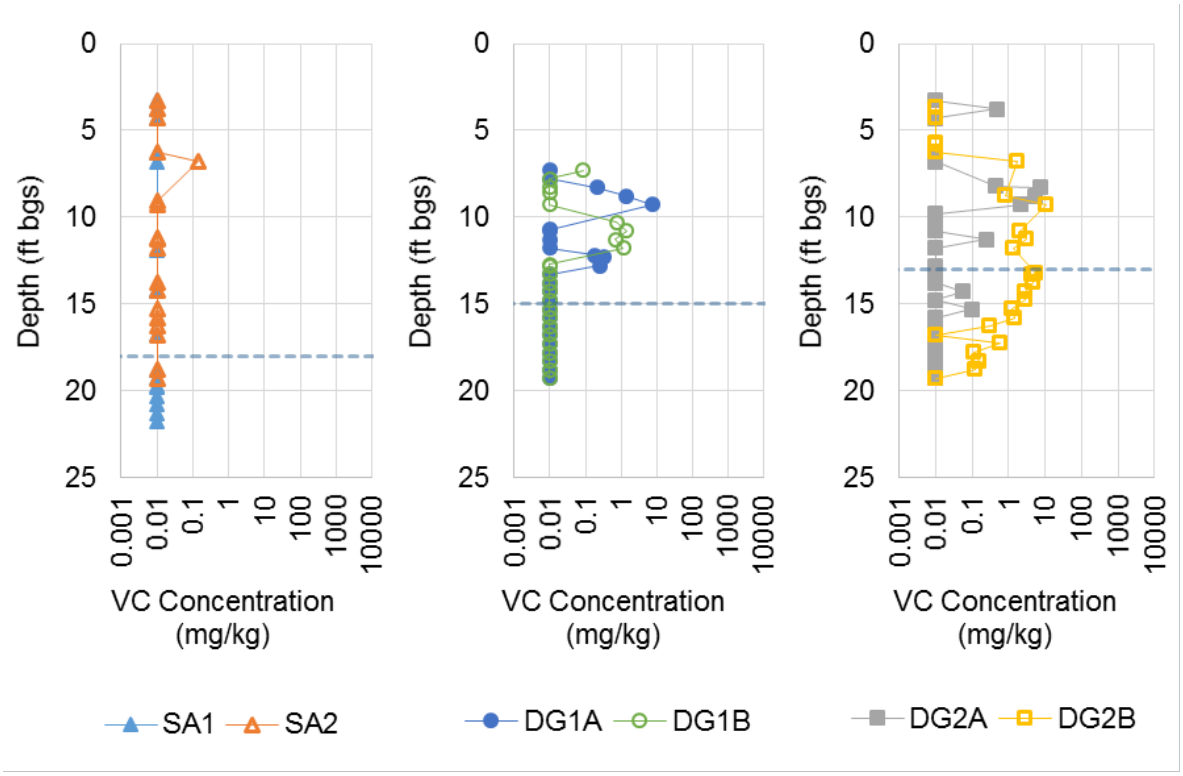

Figure 30. Concentration Data for VC (methanol extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Gaseous Organics

Summary data are shown for gaseous organics, including methane (Figure 31), ethane (Figure 32), ethylene (Figure 33), and acetylene (Figure 34). Within each figure, C_3 data are shown for source-area locations (left); downgradient transect DG1, which includes two locations oriented toward MW10 (center); and downgradient transect DG2, which includes two locations oriented toward MW02 (right). The measured aqueous-extract concentrations were converted to a total-sample basis for presentation.

Methane is not considered a primary product of TCE degradation, but is a key indicator for microbial processes and redox conditions. Methane was detected in all samples (with two exceptions). In source-area samples, methane concentrations are relatively consistent over the mixed-soil depth interval, ranging from 1.7 to 21 mg/kg. In downgradient transect DG1, methane concentrations are relatively consistent in shallow samples (i.e., in samples of <12 ft bgs in location DG1A and <14 ft bgs in DG1B), and exhibit a general trend of an exponential decline versus depth in deeper samples. Maximum measured methane concentrations in DG1A and DG1B are 11.4 and 11.8 mg/kg, respectively. In both of the DG1 locations, methane concentrations decline by approximately two orders of magnitude in a depth interval of approximately 10 ft. In downgradient transect DG2, methane concentrations are relatively consistent in shallow samples (< 9 ft bgs) but lesser values are observed in DG2A (maximum = 1.1 mg/kg) than in DG2B (maximum = 4.4 mg/kg). In transect DG2 locations, methane concentrations exhibit general declining trends versus depth in deeper samples (the declining trends observed in DG2 locations are less pronounced than those observed in the DG1 locations).

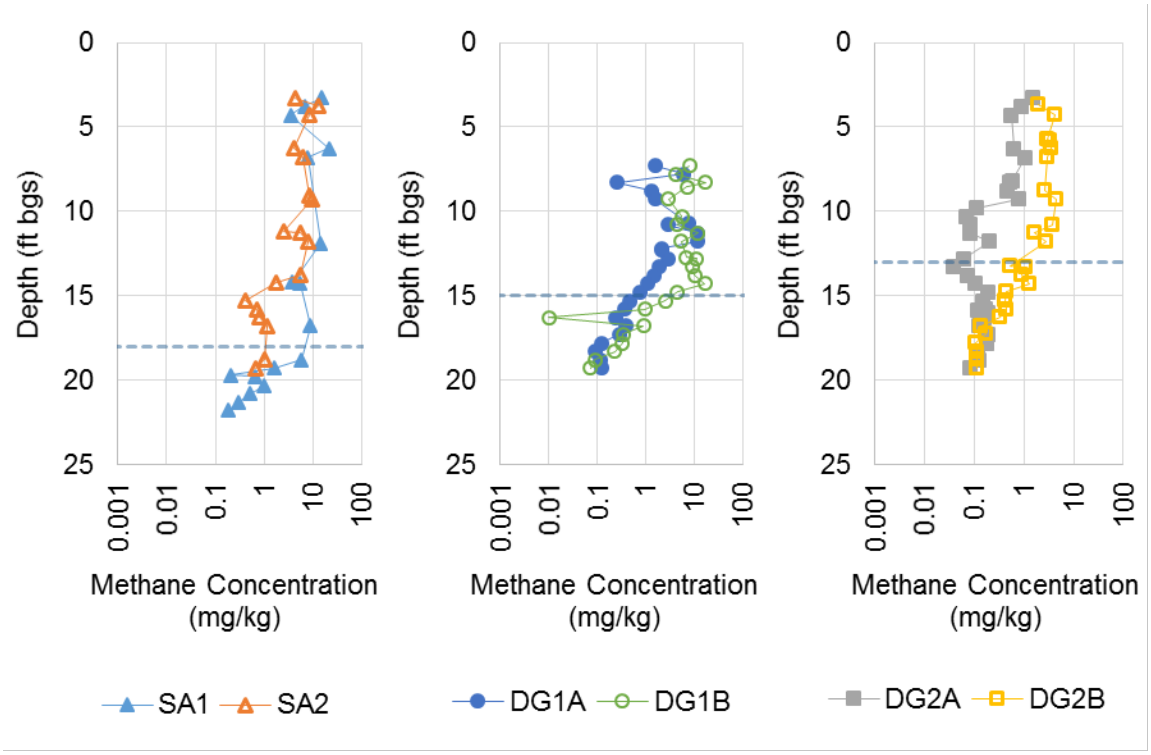

Figure 31. Concentration Data for Methane (aqueous extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Ethane was detected in most samples, including those collected from within or downgradient of the mixed-soil zone. In source-area samples, higher ethane concentrations are typically observed in location SA2 (maximum = 0.6 mg/kg) than in SA1 (maximum = 0.09 mg/kg); in both locations, concentrations span approximately one order of magnitude. In downgradient transect DG1, ethane concentrations exhibit a similar trend in locations DG1A and DG1B. In both locations, ethane concentrations follow sideways "V" shaped pattern. The maximum ethane concentrations in DG1A and DG1B are 11 and 8 mg/kg, respectively. In downgradient transect DG2, the highest ethane concentrations occur in shallow samples in location DG2A, whereas in DG2B the highest concentrations occur in deeper samples. The maximum ethane concentrations in DG2 are 0.3 mg/kg and 1.0 mg/kg in DG2A and DG2B, respectively.

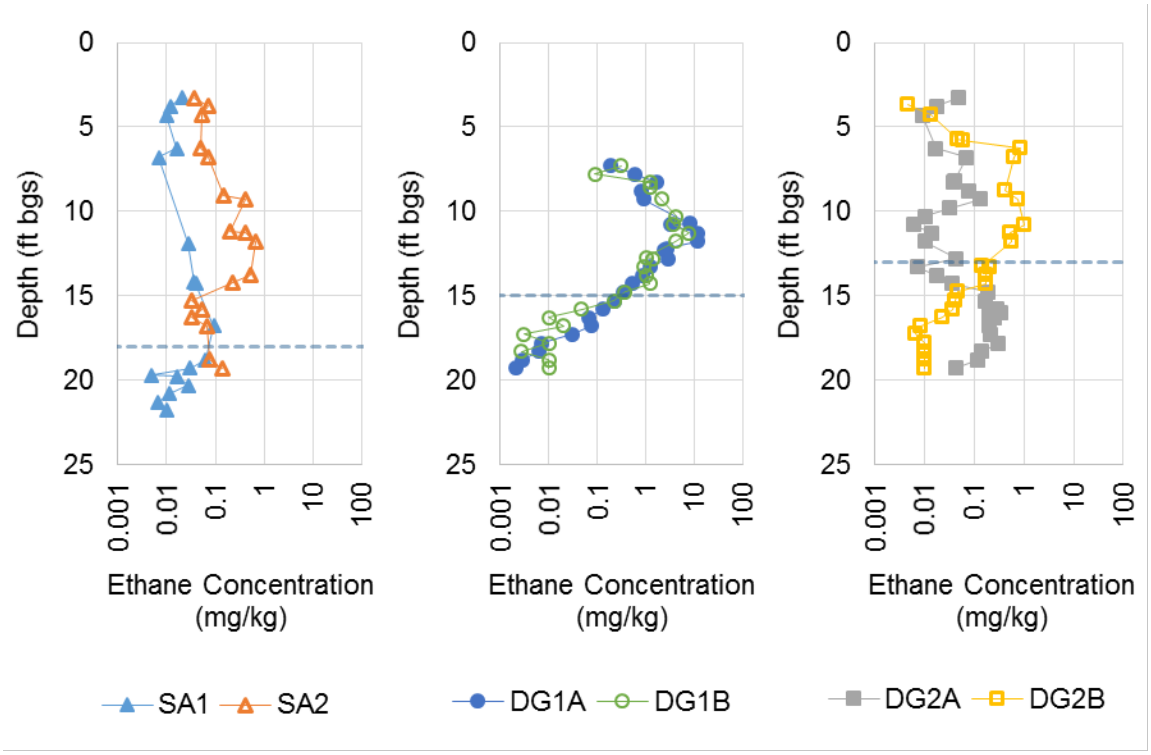

Figure 32. Concentration Data for Ethane (aqueous extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Ethylene is an intermediate product of TCE degradation that is less stable than methane or ethane, and was therefore detected in fewer samples. In source-area samples, ethylene was below detection limits (0.01 mg/kg) in all samples from location SA1, and was only detected within a discrete interval in SA2 (maximum = 1.4 mg/kg). In downgradient transect DG1, ethylene concentrations exhibit a similar trend in locations DG1A and DG1B; that is, a band of elevated ethylene occurs across a discrete depth interval, and is otherwise below detection limits. The maximum ethylene concentrations in DG1A and DG1B are 5.9 and 6.5 mg/kg, respectively. In downgradient transect DG2, ethylene concentrations occur across a wider depth interval, primarily in deeper samples (i.e., > 8 ft bgs). The maximum ethylene concentrations in DG2 are 0.2 mg/kg and 3.1 mg/kg in locations DG2A and DG2B, respectively.

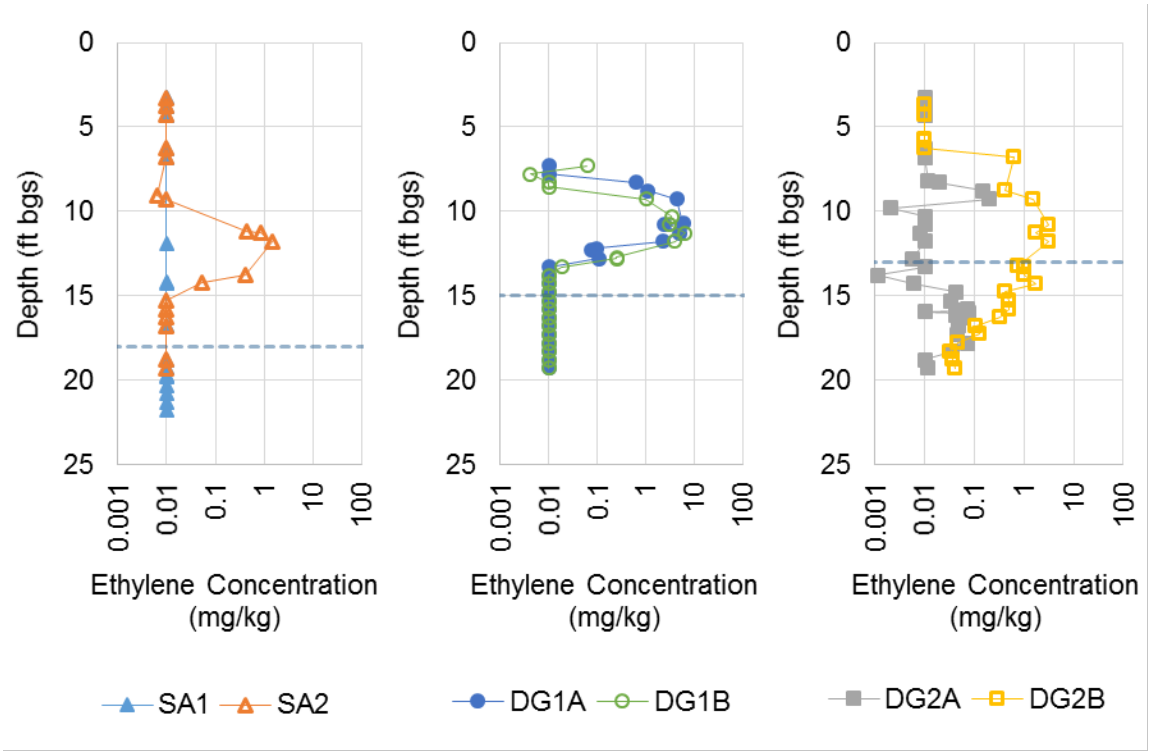

Figure 33. Concentration Data for Ethylene (aqueous extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Acetylene an intermediate product of TCE degradation that is primarily formed via abiotic degradation (Brown et al. 2009); once formed, acetylene is readily degradable (Arnold and Roberts 2000, He et al. 2015). Therefore, acetylene was only detected in a small number of locations, presumably where it was being actively produced. Acetylene was below detection limits (0.01 mg/kg) in all samples collected from the source area (i.e., locations SA1 or SA2) and downgradient transect DG1 (locations DG1A or DG1B). However, acetylene was detected in several samples from one of the locations in transect DG2 (location DG2A). Acetylene detections in DG2A occurred primarily in deep samples (i.e., depth >8 ft bgs); the maximum detected acetylene concentration in DG2A was 0.02 mg/kg.

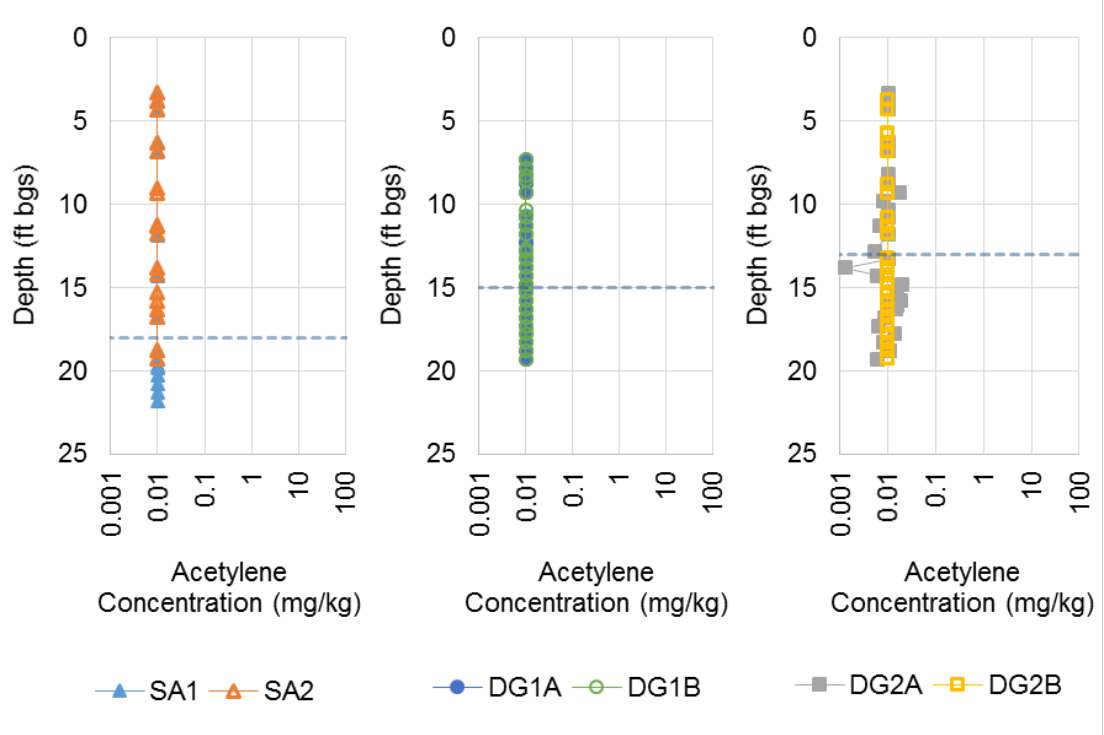

Figure 34. Concentration Data for Acetylene (aqueous extract).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

5.7.2 Inorganics

Summary data are shown for inorganics, including chloride (Figure 35), sulfate (Figure 36), and ferrous iron (Figure 37). Tabulated data for these and additional analytes, including nitrate and total iron, are shown in Appendix H. Within each figure, results are shown for source-area locations (left); downgradient transect DG1, which includes two locations oriented toward MW10 (center); and downgradient transect DG2, which includes two locations oriented toward MW02 (right). The measured aqueous-extract concentrations were converted to pore-water concentrations.

Chloride is present in groundwater due to both naturally occurring sources and degradation of chlorinated solvents. In source-area samples, elevated chloride is observed in SA2, which is located in the portion of the source area in which TCE DNAPL was inferred prior to treatment.

The maximum chloride levels in SA1 and SA2 were 290 and 3300 mg/L, respectively. In downgradient transect DG1, chloride concentration is relatively consistent near the source area (location DG1A) but varies over several orders of magnitude nearer the creek (DG1B); the maximum chloride concentrations in DG1A and DG1B are 1300 and 1000 mg/L, respectively. In downgradient transect DG2, chloride concentrations exhibit a minor increasing trend versus depth. The maximum chloride concentrations in DG2A and DG2B are 1600 and 550 mg/L, respectively.

Sulfate typically occurs in groundwater due to natural sources, but human-made sources may also affect groundwater concentrations. In all locations, sulfate concentrations vary by multiple orders of magnitude; sulfate-concentration trends versus depth are generally sporadic. The maximum sulfate levels in SA1 and SA2 were 760 and 470 mg/L, respectively. The maximum sulfate concentrations in DG1A and DG1B are 3400 and 5400 mg/L, respectively. The maximum sulfate concentrations in DG2A and DG2B are 6700 and 3300 mg/L, respectively. The elevated sulfate levels may suggest oxidation of reduced sulfur species after extraction of the frozen core; the aqueous extraction samples may have been exposed to oxygen during removal of samples for organics analysis (Section 5.7.1). Subsequent work will be conducted to evaluate this data.

Ferrous iron (Fe[II]) typically occurs in groundwater due to natural sources, but human-made sources may also affect groundwater concentrations. Fe(II) concentrations exhibit depth-discrete concentration spikes, indicating levels in which iron-reducing conditions may be occurring. The maximum Fe(II) levels in SA1 and SA2 were 6.5 and 48 mg/L, respectively. The maximum Fe(II) concentrations in DG1A and DG1B are 62 and 25 mg/kg, respectively. The maximum Fe(II) concentrations in DG2A and DG2B are 560 and 110 mg/kg, respectively.

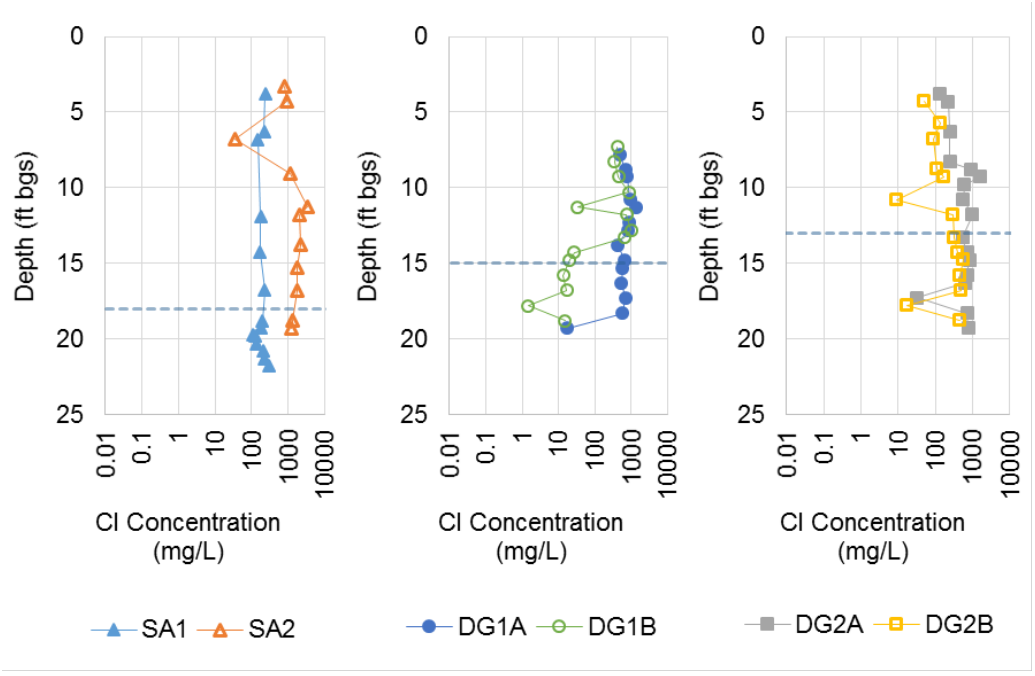

Figure 35. Concentration Data for Chloride.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

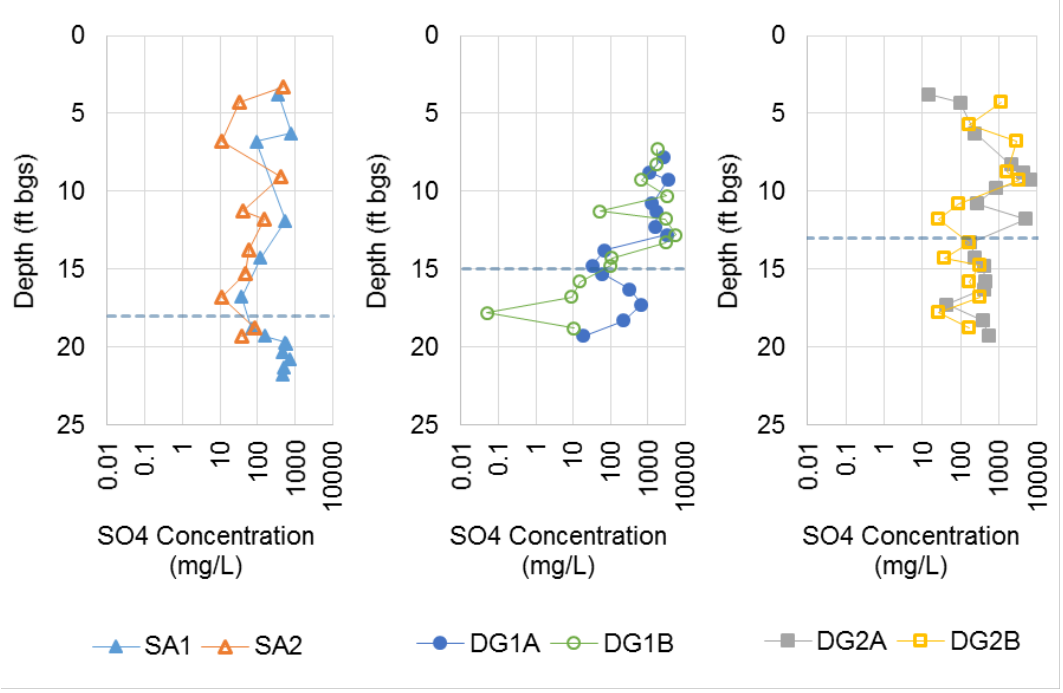

Figure 36. Concentration Data for Sulfate.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

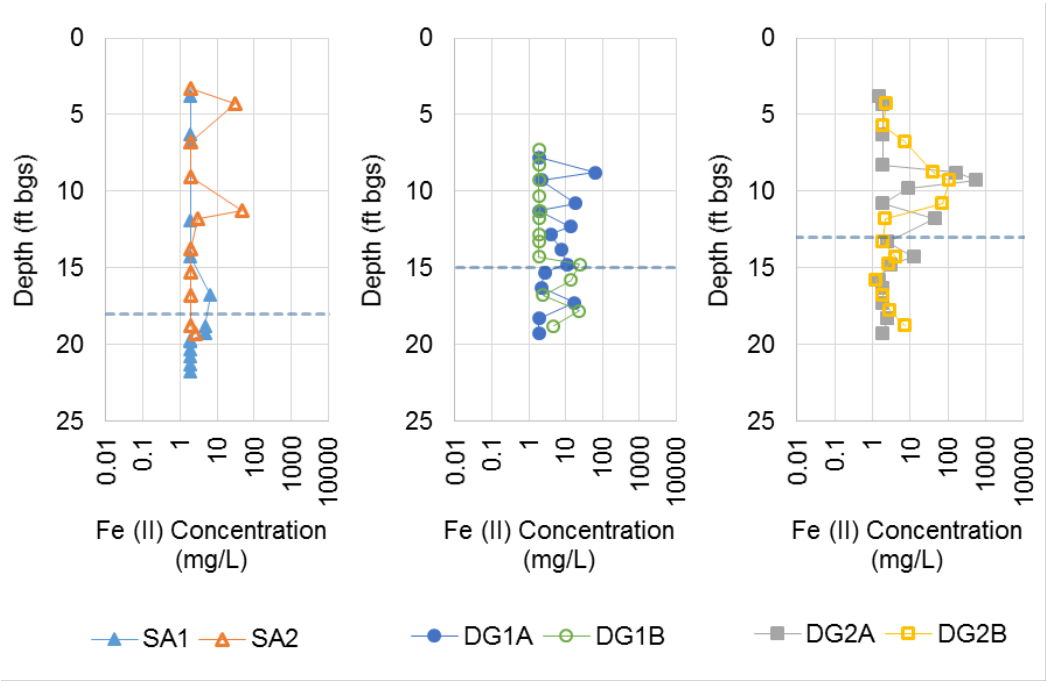

Figure 37. Concentration Data for Fe(II).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

5.7.3 Soil Properties

Soil properties included bulk density, organic carbon, clay content, and hydraulic conductivity.

Bulk Density.

Bulk density was calculated based on data collected during the aqueous-extraction procedures. Results are shown on Figure 38 as total (wet soil basis) bulk density.

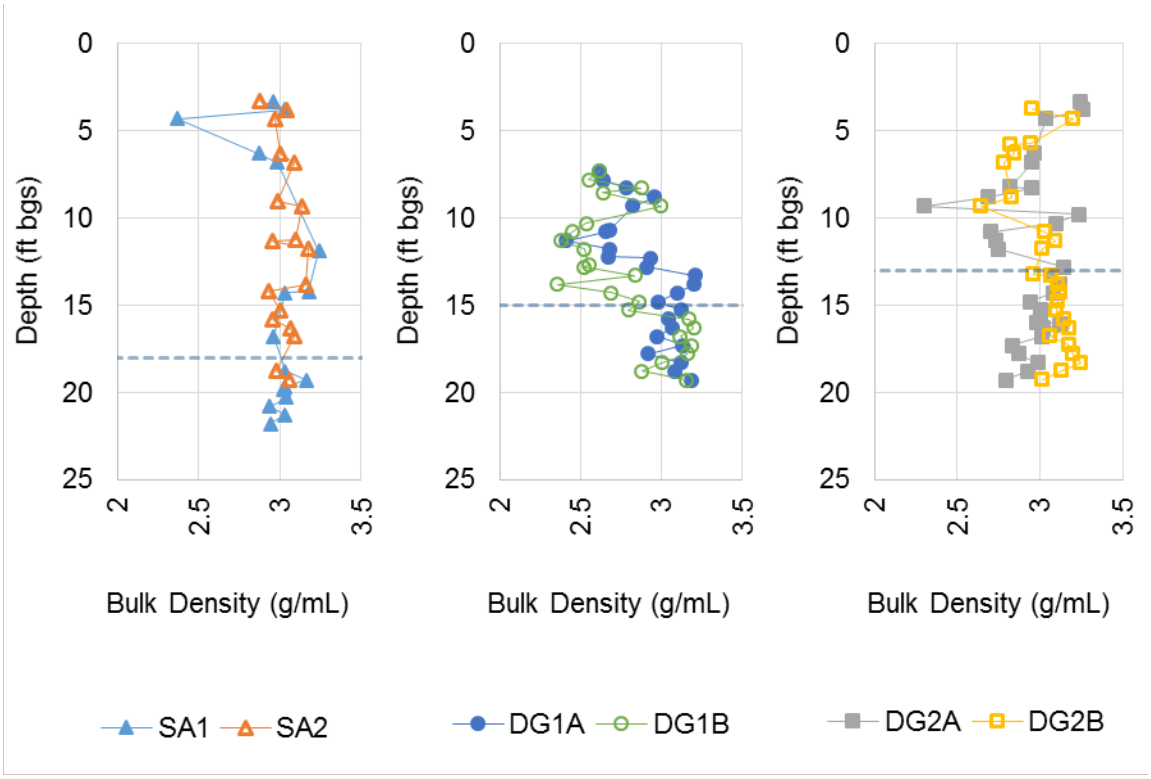

Figure 38. Bulk Density Data (wet sample basis).

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Fraction Organic Carbon.

Data resulting from f_{oc} analysis are shown in Figure 39. In the ZVI-Clay mixed-zone soils, f_{oc} values ranged from 0.2 to 2.8%. In the downgradient locations, f_{oc} values ranged from 0.1 to 0.6% in the underlying clay. In the shallower silt/sand soils, f_{oc} values were relatively higher with typical values ranging from 1 to 6%. The higher f_{oc} values in the shallow soils corresponds with the typically brown color of the soils. A very high f_{oc} value was measured in one sample (26% at DG2A at 9.29 ft bgs); this sample was observed to consist of weathered woody debris, which explains the high f_{oc} value.

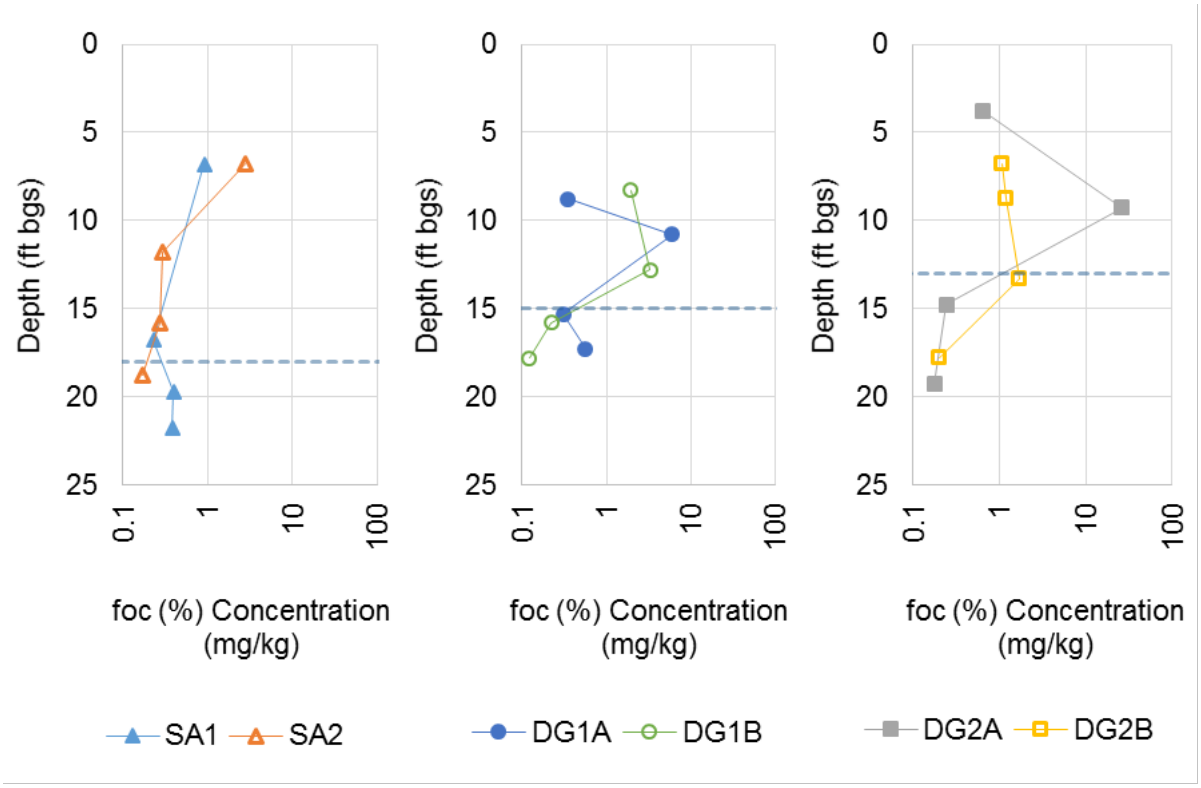

Figure 39. Total Organic Carbon Data.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

Clay Content.

A semi-quantitative method was used to determine relative clay content. The method was based on settlement in the aqueous extract vials after 1 and 3 days of settlement time. The method resulted in a semi-quantitative "Clay Content Index" value between 0 and 3, where 0 indicates minimal clay in the sample and 3 indicates a high clay content. The Clay Content Index values resulting from this analysis are shown in Figure 40.

In the source-area samples, consistently high Clay Content Index values were measured over the mixed-soil zone in location SA1, with values ranging from 2.7 to 3.0. The Clay Content Index values were much more variable in SA2, ranging from 0 to 2.0 in the mixed depth interval. High Clay Content Index values are expected in the mixed zone, as the soils have been homogenized and admixed with bentonite. The soils in the area of SA2 were also admixed with a higher ZVI content (target 3%) than SA1 (target 1% ZVI). The higher ZVI content may have affected geochemistry in a fundamental manner (e.g., charge balance) that affected clay settlement rates.

In the downgradient locations, the Clay Content Index values provide an indication of geologic heterogeneity, including the transition between overlying transmissive soils and underlying low-k clays. In transects DG1 and DG2, the transitions between low- and high-clay content soils occur at approximately 15 and 13 ft bgs, respectively (in both of these transects, high Clay Content Index value are observed in shallower strata, but the bulk transition occurs at the approximate depth indicated). In soils above these transitional depths, Clay Content Index is characterized by (a) relatively low values of (2 or less) over much of the depth interval and (b) a high degree of heterogeneity. In samples below these transitional depths, the Clay Content Index is characterized by (a) relatively high values (at or near 3) and (b) a lesser degree of heterogeneity.

The Clay Content Index values are the primary basis for the dashed lines, indicating geologic transition between the clay aquitard and overlying soils, presented in figures throughout Section 5.7.

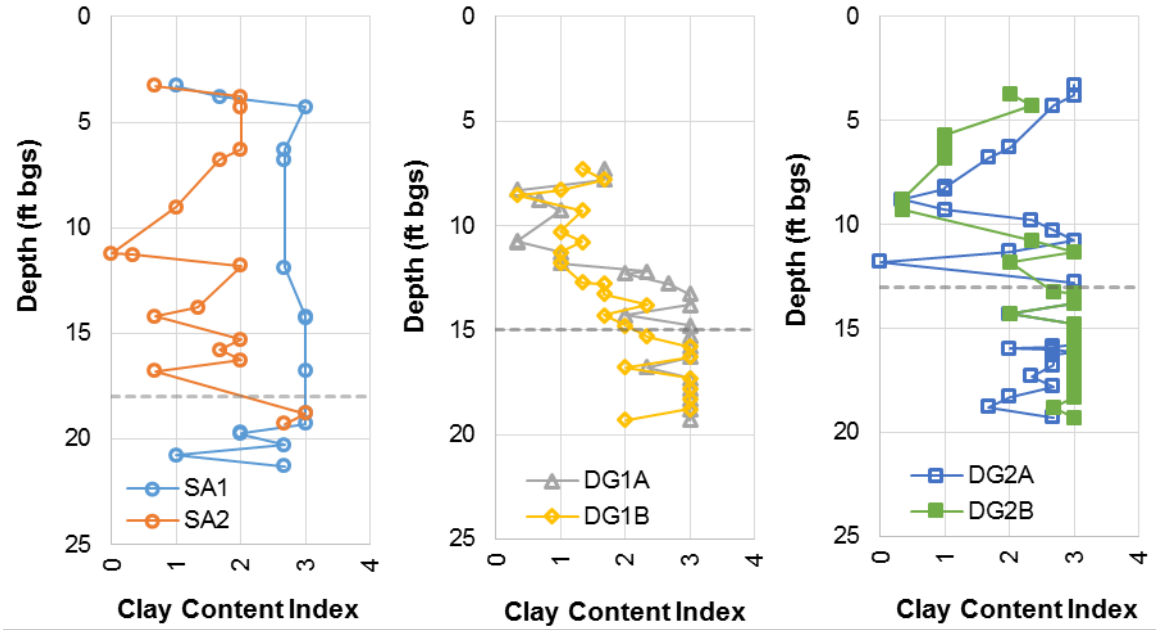

Figure 40. Clay Content Indices versus Depth.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

5.7.4 Hydraulic Conductivity

Hydraulic conductivity testing was conducted on a subset of 11 samples, selected to represent different geology observed at the site. Results of the hydraulic conductivity testing are presented in Table 7. Results ranged from 1.0×10^{-6} to 1.2×10^{-2} cm/sec. In the ZVI-Clay mixed soil zone, hydraulic conductivity ranged from 5.6×10^{-6} to 9.2×10^{-6} cm/sec. In downgradient locations, hydraulic conductivity ranged from 1.0×10^{-6} to 1.1×10^{-4} cm/sec in the underlying clay; in the overlying "transmissive" zone, measured hydraulic conductivity ranged from 3.3×10^{-4} to 1.2×10^{-2} cm/sec.

Table 7. Hydraulic Conductivity Results Summary

Location	Depth	Hydraulic Conductivity (cm/sec)	log K*	Notes
SA1	6.79	9.2E-06	-5.0	
SA1	21.29	5.6E-06	-5.3	
DG1A	8.29	1.2E-02	-1.9	
DG1A dup	8.29	1.2E-02	-1.9	Duplicate analysis
DG1A	11.29	3.3E-04	-3.5	
DG1A	13.29	2.0E-06	-5.7	
DG1A	15.79	1.0E-06	-6.0	
DG1A	18.29	1.1E-04	-4.0	Space in sample noted/ preferential flow?
DG1A	17.79	1.0E-05	-5.0	
DG1B	11.29	2.0E-03	-2.7	
DG1B dup	11.29	1.9E-03	-2.7	Duplicate analysis
DG1B	18.79	6.9E-06	-5.2	

Notes:

K = hydraulic conductivity

5.7.5 Microbiological Characterization

Table 8 shows relative abundance of select dechlorinating bacteria, including *Dehalococcoides*, *Dehalogenimonas*, and *Dehalobacter* (Manchester et al. 2012, Hug et al. 2013). Samples in which the total abundance of dechlorinating bacteria was greater than 1% of the total Bacteria are highlighted in Table 8. For comparison, concentrations of chlorinated ethylenes (TCE, *c*DCE, and VC) and gaseous products (acetylene, ethylene, and ethane) are also shown.

Overall, correlations between dechlorinating bacteria and concentration data were not observed. In most samples, relatively low quantities are apparent for both total dechlorinating bacteria (i.e., <0.48%) and chlorinated ethylene concentrations (i.e., <0.3 mg/kg). However, it is noteworthy that dechlorinating bacteria were detected in most samples. Sample locations of particular interest include the following:

- In SA2, *Dehalococcoides* were detected at 20% (11.29 ft bgs) and 2.7% (15.29 ft bgs) in locations containing TCE concentrations of 0.048 mg/kg or less. This portion of the source area was inferred to contain DNAPL prior to remediation; thus, the elevated *Dehalococcoides* may reflect historical biodegradation.

- Another sample of interest is from location DH2A at 9.29 ft bgs, which contained elevated *Dehalococcoides* (6%) and *Dehalogenimonas* (43%); elevated concentrations of TCE (670 mg/kg), *c*DCE (43 mg/kg), and VC (2.1 mg/kg) were detected, as well as gaseous products, including acetylene (0.017 mg/kg) and ethylene (0.2 mg/kg). The elevated levels of dechlorinating bacteria and presence of chlorinated ethylenes throughout the biodegradation pathway suggest active biodegradation at this location.

- In location DG2B at 9.29 ft bgs, elevated *Dehalococcoides* (9.9%) and *Dehalogenimonas* (7.5%) were detected. TCE was non-detect (<0.01 mg/kg) but elevated quantities of *c*DCE (5.2 mg/kg), VC (11 mg/kg), and ethylene (1.6 mg/kg) were detected. The presence of degradation products suggest active biodegradation at this location.

- In location DG2B at 14.79 ft bgs, only low quantities of *Dehalococcoides* (0.1%) and *Dehalobacter* (0.2%) were detected, despite elevated concentrations of TCE (35 mg/kg), *c*DCE (8.3 mg/kg), VC (2.8 mg/kg), and ethylene (0.43 mg/kg). Active degradation may be suggested by these data, but the higher concentration of parent compounds (TCE and cDCE) relative to products (VC and ethylene) suggest a slower rate, when compared to the shallower sample (DG2B at 9.29 ft bgs, described in the previous bullet).

The DNA recovery was limited in several samples, particularly in samples from low-*k* zones (Appendix G). Thus, the conclusions that can be drawn at Site 17 based on currently available microbial data are limited. However, improved preservation of microbial properties presents a key potential advantage of collecting soil cores cryogenically. To address the DNA recovery limitations, improving DNA recovery from soil samples with variable properties (e.g., in the presence of NAPL or in soils with unusual geochemical properties, such as high iron content) is a current area of active research.

Additional information on the Site 17 microbial characterization, including order- and phyla-level results, are provided in Appendix G.

Table 8. Comparison of Dehalogenator Abundance to Chemical Concentration Data

Location	Depth	*Dehalococcoides spp.*	*Dehalogenimonas spp.*	*Dehalobacter spp.*	Total	TCE	cDCE	VC	Acetylene	Ethylene	Ethane
--	ft bgs	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SA1	6.29	0.13	0.16	0	0.29	0.29	ND	ND	ND	ND	0.016
SA1	6.79	0.1	0.1	0	0.2	0.2	0.17	ND	ND	ND	0.0068
SA1	11.88	0.2	0.1	0	0.3	0.17	ND	ND	ND	ND	0.028
SA1	19.79	0	0	0	0	0.12	ND	ND	ND	ND	0.016
SA2	6.29	0	0	0	0	ND	0.15	ND	ND	ND	0.049
SA2	11.29	20.17	0.65	0.58	21.4	0.048	ND	ND	ND	0.87	0.4
SA2	15.29	2.71	0.4	0.06	3.17	0.036	ND	ND	ND	ND	0.033
DG1A	7.79	0.25	0.2	0.03	0.48	0.018	ND	ND	ND	ND	0.57
DG1A	11.29	0.12	0.27	0	0.39	ND	ND	ND	ND	5.1	11
DG1A	11.79	0.08	0.24	0	0.32	0.011	ND	ND	ND	2.2	11
DG1A	17.79	0.1	0	0	0.1	ND	ND	ND	ND	ND	0.0072
DG1A	18.29	0.7	0.9	0	1.6	ND	ND	ND	ND	ND	0.0064
DG1B	7.29	0.48	0	0	0.48	ND	ND	0.086	ND	0.062	0.31
DG2A	6.29	0.1	0.02	0	0.12	ND	ND	ND	ND	ND	0.017
DG2A	9.29	6	43.3	0	49.3	670	43	2.1	0.017	0.2	0.14
DG2B	9.29	9.9	7.5	0.18	17.58	ND	5.2	11	ND	1.6	0.77
DG2B	14.79	0.1	0	0.2	0.3	35	8.3	2.8	ND	0.43	0.046

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Notes:

- Genus-level percent abundance of total Bacteria is presented for *Dehaloccoides*, *Dehalogenimonas*, and *Dehalobacter*.
- Highlighted rows indicate locations with total abundance of dehalogenator abundance (i.e., *Dehaloccoides* + *Dehalogenimonas* + *Dehalobacter*) greater than 1%.

5.7.6 ZVI Content

ZVI content was evaluated on a depth-discrete basis on samples from three locations: SA2, DG2A, and DG2B; ZVI content versus depth is shown on Figure 41. Location SA2 occurs in the excess-ZVI portion of the mixed-soil zone (Figure 19). According to QA/QC samples collected in November 2012, the delivered ZVI content ranged from 2.9% to 4.3% (the average was 3.5%) within the excess-ZVI area (Table 2).

Results of the ZVI-content analysis conducted herein (Figure 41) suggest that the measured ZVI content was substantially higher within the mixed-soil zone (SA2) than in downgradient locations (DG2A and DG2B). Within the mixed-soil zone, ZVI content values up to 2.8% were measured. This indicates that ZVI persists, four years after remediation was implemented. The ZVI content in SA2 is low (<0.08%) through a depth of about 11 ft bgs; ZVI delivery only targeted a depth interval of 8 to 18 ft bgs (Section 4.1.1). In samples collected below 11 ft bgs, variability in the ZVI distribution is observed (Figure 41). Sudden increases, followed by downward-tailing trends, are observed at depths of 11.79 and 16.29 ft bgs. A particularly low ZVI content (0.001%) is noted at 15.29 ft bgs. The variable ZVI-content values may relate to non-uniform ZVI consumption rates or non-homogeneous delivery of ZVI. Post-mixing ZVI-content values (Table 2), although collected with moderately low-resolution sampling (minimum 2-ft intervals), were relatively uniform. This suggests that variable ZVI-consumption rates are most likely the cause of variable ZVI contents, four years after remediation. The ZVI content was measured at 0.03% or less in all downgradient samples. The trivial amount of ZVI measured downgradient is expected, as ZVI is not typically found in nature and no ZVI was delivered to these locations.

A qualitative indication of the redox state of iron in the former source zone is presented in Figure 42. This shows a photograph of a soil clod, comprising soils from location SA2, approximately two days after sample collection from this location. The surface of the clod was exposed to atmospheric oxygen, which oxidized iron particles and formed the telltale reddish color of iron oxides. The inside of the clod was protected from atmospheric oxygen, thus remained representative of subsurface redox conditions. Upon breaking the clod open, a grey color was apparent. The grey color of the unexposed iron suggests that iron persists in a reduced redox state, possibly comprising ZVI or magnetite.

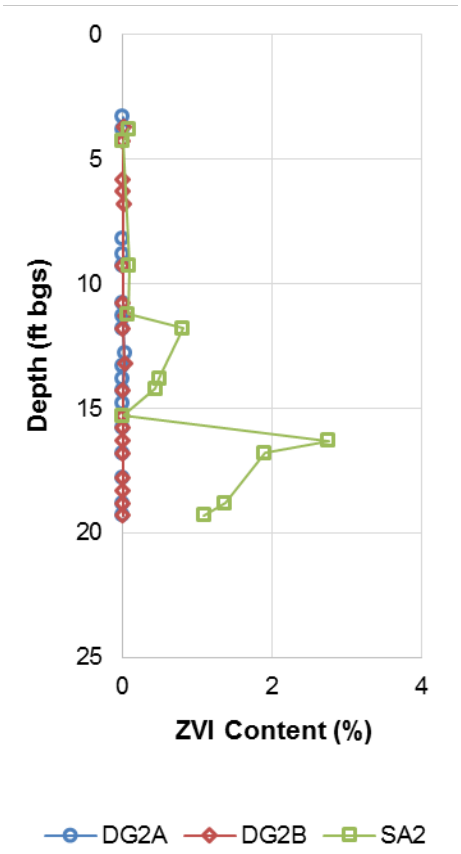

Figure 41. ZVI Content

Figure 42. Photo of soil clod, illustrating iron-induced color change before and after exposure to oxygen.

5.7.7 Reactivity Testing

Results of the reactivity testing are summarized in Table 9. Reactivity was evaluated using one sample from each of the six soil-core locations. The reactivity testing likely excludes potential biodegradation, as microbes are unlikely to survive the cryogenic freezing process. Thus, the results herein are considered to represent the abiotic degradation potential. The results suggest that degradation potential exists within the treated soil zone. Both locations within the former source area, which was remediated via admixing soils with ZVI, exhibited the potential to achieve abiotic degradation of TCE. The reaction potential appeared stronger in location SA1, despite this location having been mixed with a lesser target ZVI content than location SA2, where excess ZVI (>3%) was added. Additional discussion of this data is presented in Section 6.3.2.

Table 9. Reactivity Results Summary

Location	Depth	Reactivity noted?	Notes
SA1	16.79	Yes	Reactivity potential appears strong
SA2	15.29	Yes	Reactivity potential appears moderate
DG2B	14.79	No	No products noted
DG2A	14.79	No	No products noted
DG1A	14.79	No	No products noted
DG1B	14.79	No	No products noted

5.7.8 External Laboratory Analysis

Six frozen-soil samples, one from each soil-core location, were sent to an external laboratory with the objectives of (a) comparing results to an external laboratory, and (b) identifying other organic compounds that may be present. The external analysis results are summarized and compared to the results generated by the laboratory at CSU in Table 10. Each comparison shown in Table 10 represents three quarters from the same frozen sample disc ("puck"); thus, the three results represent different soil samples collected from the same depth. Results are shown in Table 10 for analytes that were detected above reporting limits in the EPA 8260 analysis. CSU results for both methanol- and aqueous-extract samples are shown.

The external analysis resulted in detections above reporting limits for seven analytes that were not included in the CSU analytical suite: acetone, benzene, 2-butanone, chlorobenzene, dichloromethane (DCM), methyl tert-butyl ether (MTBE), and 1,1,2-trichloroethane (112-TCA). Of these, only acetone and DCM were detected at concentrations greater than 0.1 mg/kg. The maximum detected concentrations for DCM and acetone were 4.6 and 0.72 mg/kg, respectively; both of these maximum detection occurred in DG1B.

The comparison of external laboratory results to CSU analytical results was mixed. For analytes present at concentrations at or below detection limits, the results were generally comparable. In samples containing relatively high concentrations of TCE and *c*DCE, which were collected from locations DG2A and DG2B, the CSU results for in both methanol- and aqueous-extract samples were higher than the external laboratory results. The different results may reflect heterogeneous distribution within the soils. Alternatively, the higher concentration data in the CSU-analyzed samples may reflect losses occurring during extra handling and storage of the samples prior to analysis by the external laboratory (as discussed in Section 5.6.8). If the external laboratory samples had been prepared at the time of processing, at the same time as the CSU-analyzed samples, results may have been more similar.

Overall, the results of the external laboratory analysis provided the following insights:

- Organic analytes, aside from those analyzed by CSU, were typically not present at elevated concentrations (i.e., detections at greater than 0.1 mg/kg were rare). Analytes that were present at greater than 0.1 mg/kg, which included DCM and acetone, are relatively common co-contaminants at chlorinated solvent sites.

- Extraction of samples immediately after processing, without re-packaging and freezing, may be important in preserving volatile analytes.

Table 10. Comparison of External Laboratory to CSU Analytical Results

	SA1 - 16.79 ft bgs			SA2 - 15.29 ft bgs			DG1A - 14.79 ft bgs		
	EPA 8260*	Meth Ext**	Aq Ext.***	EPA 8260*	Meth Ext**	Aq Ext.***	EPA 8260*	Meth Ext**	Aq Ext.***
PCE	ND	ND	--	ND	ND	--	ND	ND	--
TCE	0.006	ND	ND	ND	0.036	ND	0.046	ND	ND
cDCE	ND	ND	ND	ND	ND	ND	0.003	ND	ND
tDCE	ND	ND	--	ND	ND	--	ND	ND	--
11-DCE	ND	ND	--	ND	ND	--	ND	ND	--
VC	ND	ND	ND	ND	ND	ND	0.002	ND	ND
112-TCA	ND	--	--	ND	--	--	ND	--	--
2-Butanone	ND	--	--	0.021	--	--	ND	--	--
Acetone	0.017	--	--	0.064	--	--	0.370	--	--
Benzene	ND	--	--	0.002	--	--	ND	--	--
Chlorobenzene	0.002	--	--	0.028	--	--	0.003	--	--
DCM	0.300	--	--	0.003	--	--	0.950	--	--
MTBE	0.027	--	--	0.039	--	--	0.033	--	--

	DG1B - 14.79 ft bgs			DG2A - 14.79 ft bgs			DG2B - 14.79 ft bgs		
	EPA 8260*	Meth Ext**	Aq Ext.***	EPA 8260*	Meth Ext**	Aq Ext.***	EPA 8260*	Meth Ext**	Aq Ext.***
PCE	ND	ND	--	0.020	ND	--	0.002	ND	--
TCE	0.080	ND	ND	18.0	97.2	177	6.70	34.9	21.7
cDCE	0.003	ND	ND	3.00	1.31	3.09	4.90	8.34	6.29
tDCE	ND	ND	--	0.043	ND	--	0.032	ND	--
11-DCE	ND	ND	--	0.050	ND	--	0.004	ND	--
VC	ND	ND	ND	0.051	ND	0.055	0.590	2.83	0.709
112-TCA	ND	--	--	0.060	--	--	0.007	--	--
2-Butanone	ND	--	--	ND	--	--	0.024	--	--
Acetone	0.720	--	--	0.700	--	--	0.040	--	--
Benzene	ND	--	--	0.001	--	--	ND	--	--
Chlorobenzene	0.012	--	--	0.002	--	--	0.010	--	--
DCM	4.60	--	--	1.90	--	--	0.002	--	--
MTBE	0.042	--	--	0.052	--	--	0.032	--	--

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Notes:

* EPA 8260 analysis was conducted by ALS laboratories, following aqueous extraction at CSU

** "Meth Ext" refers to methanol-extracted samples; extraction and anlaysis conducted at CSU

*** Aq Ext" refers to aqueous-extracted samples; extraction and anlaysis conducted at CSU

ND indicates analytes that were analyzed for but were not detected

-- indicates analytes that were note analyzed for using the specific method

6.0 PERFORMANCE ASSESSMENT

The primary goal of this project was to assess long-term impacts of ZVI-Clay Soil Mixing at Site 17; this assessment included evaluating existing remediation performance data and supplementing the existing data with high-resolution multi-parameter data from soil core samples. The performance objectives involved assessment of both the remediation technology (ZVI-Clay Soil Mixing) as well as the characterization technology (C_3) that was implemented for this project. In general, the performance objectives focus on evaluation of ZVI-Clay Soil Mixing at Site 17. Where appropriate, discussion supporting of an assessment of the C_3 characterization technology is also provided. The organization of this section follows from the performance objectives defined in Section 3.0; a subsection is provided for each of the performance objectives.

6.1 PROVIDE HIGH-RESOLUTION DATA FOR KEY PARAMETERS

In order to facilitate a detailed performance assessment of ZVI-Clay Soil Mixing performance at Site 17, high resolution data was collected for a range of key biogeochemical parameters. The need for high-resolution data to improve understanding of subsurface heterogeneity, both in terms of geology and contaminant distribution, has been well documented (e.g., Sale et al. 2013). As a means to improve understanding of long-term impacts of remediation, the C_3 technology presents a unique opportunity to provide high-resolution data that represents *in situ* conditions more accurately than conventional soil coring. This performance objective was developed to supplement existing data with high-resolution data that could address data gaps identified in the CSM and enhance the assessment of long-term remediation impacts. To assess this performance objective, the data presented in Section 5 is arranged as parallel-data plots for each of the six soil-core locations; the parallel-data plots consist of side-by-side comparisons of depth-resolved data for key analytes, (Section 6.1.1). Charts are also developed to compare C_3 data directly to groundwater data from adjacent monitoring wells (Section 6.1.2). Subsequent performance objectives further address conditions within and downgradient of the treated zone.

6.1.1 Performance Assessment by Location: Parallel Data Plots

Parallel data plots, showing C_3 data for each soil-core location, are shown in Figure 43a through Figure 43f. Source-area locations are shown on Figure 43a (SA1) and Figure 43b (SA2). Data for downgradient transect DG1 are shown in Figure 43c (DG1A) and Figure 43d (DG1B). Data for downgradient transect DG2 are shown in Figure 43d (DG2A) and Figure 43f (DG2B). Each of the parallel data plots includes the following:

- Chlorinated ethylenes (TCE, *c*DCE, *t*DCE, and VC)
- Gaseous products (methane, ethane, ethylene, and acetylene)
- Inorganic analytes (chloride, nitrate, sulfate, ferrous iron, and total iron)
- Soil properties ($f_{oc,}$ hydraulic conductivity, Clay Content Index, bulk density, and ZVI)
- Geologic logs (a key is provided in Figure 43g)

To aid in summarizing the large quantity of data presented in Figure 43a through Figure 43f, a "box-and-number" system is incorporated. For areas of interest in Figure 43a through Figure 43f, a grey box and associated number is shown on the figure. A description of observations associated with each numbered box, sorted by C_3-sampling location, is presented below.

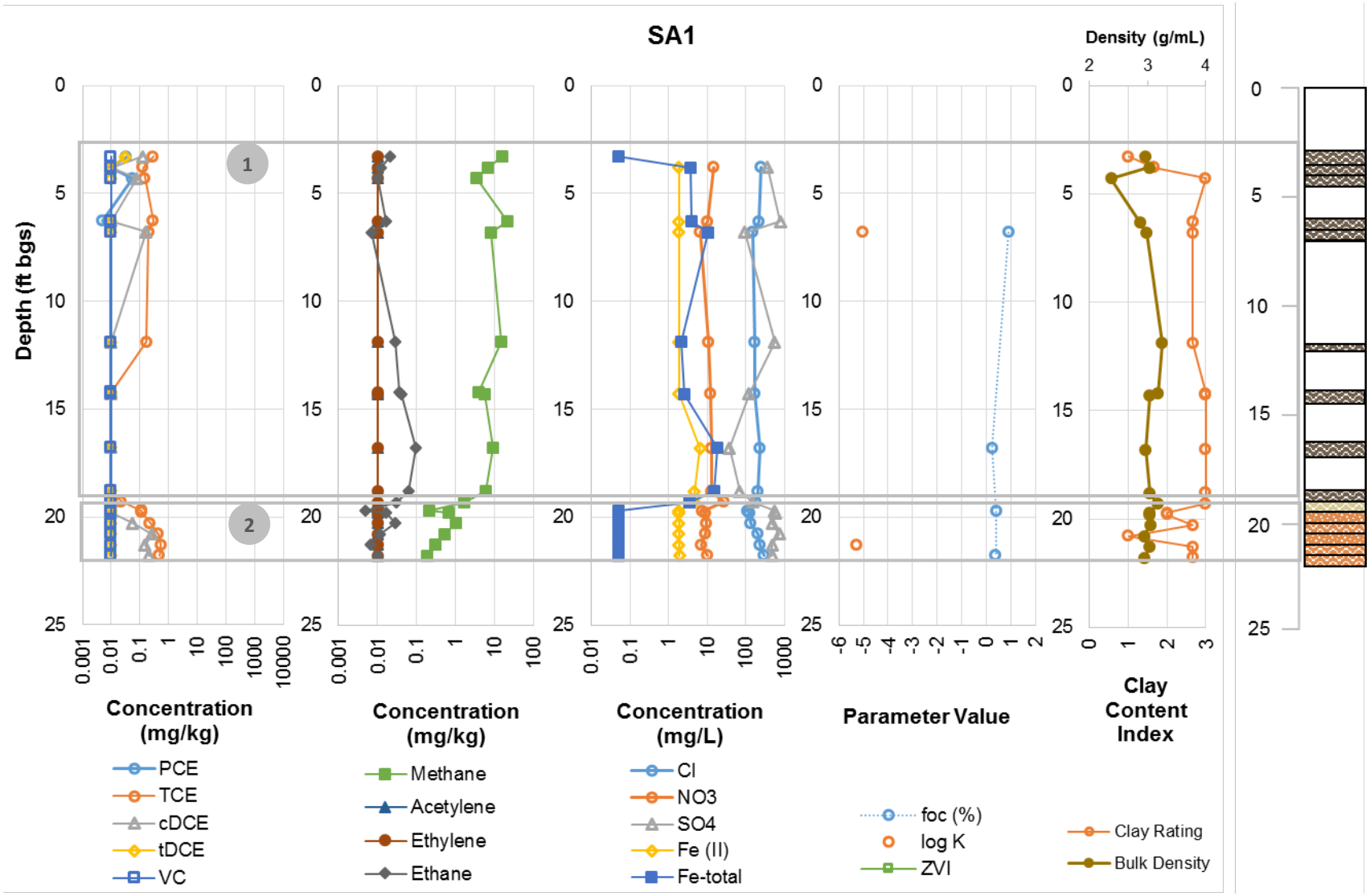

Figure 43a. Parallel Data Plots for Source-zone Location SA1.

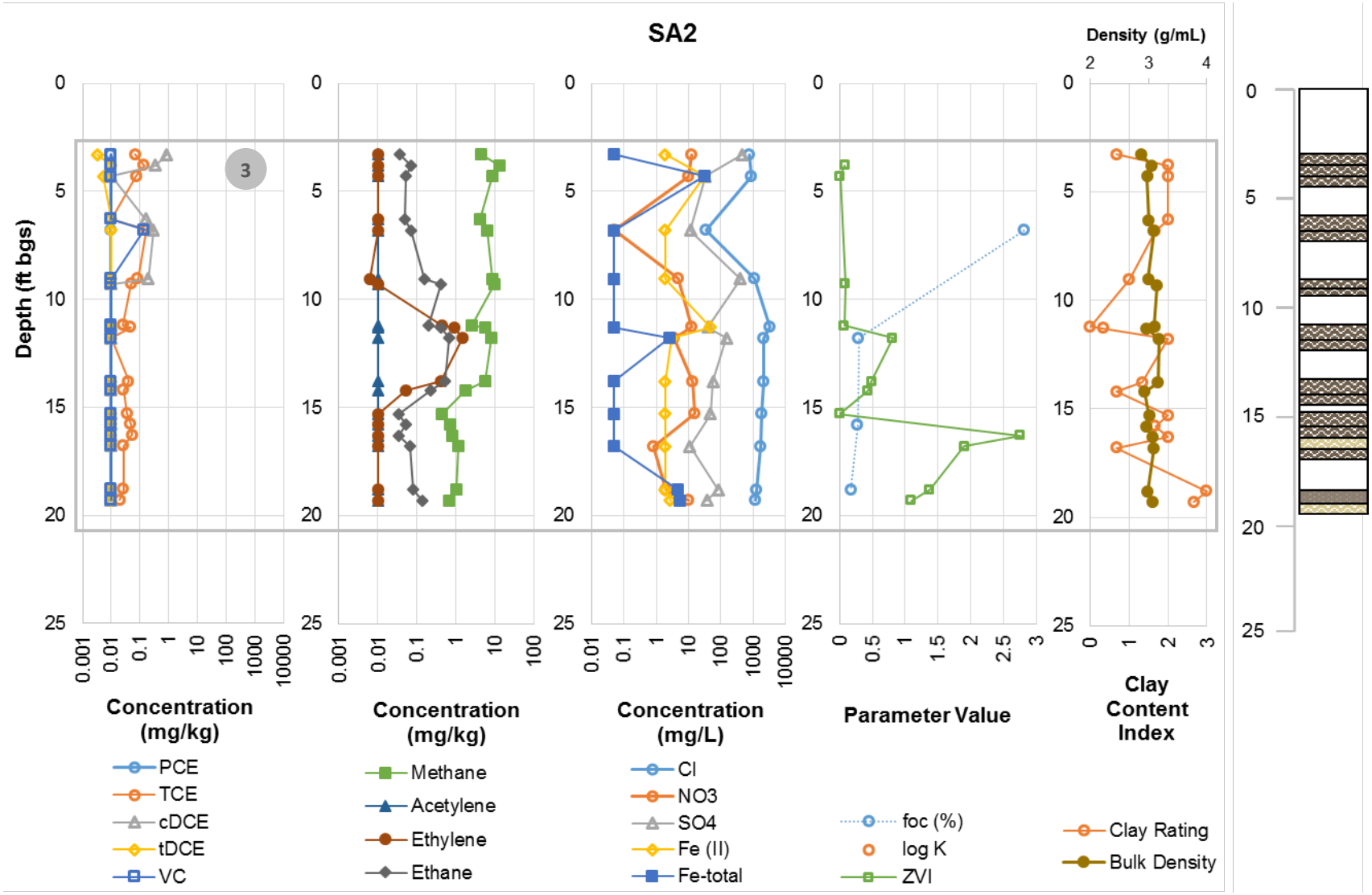

Figure 43b. Parallel Data Plots for Source-zone Location SA2.

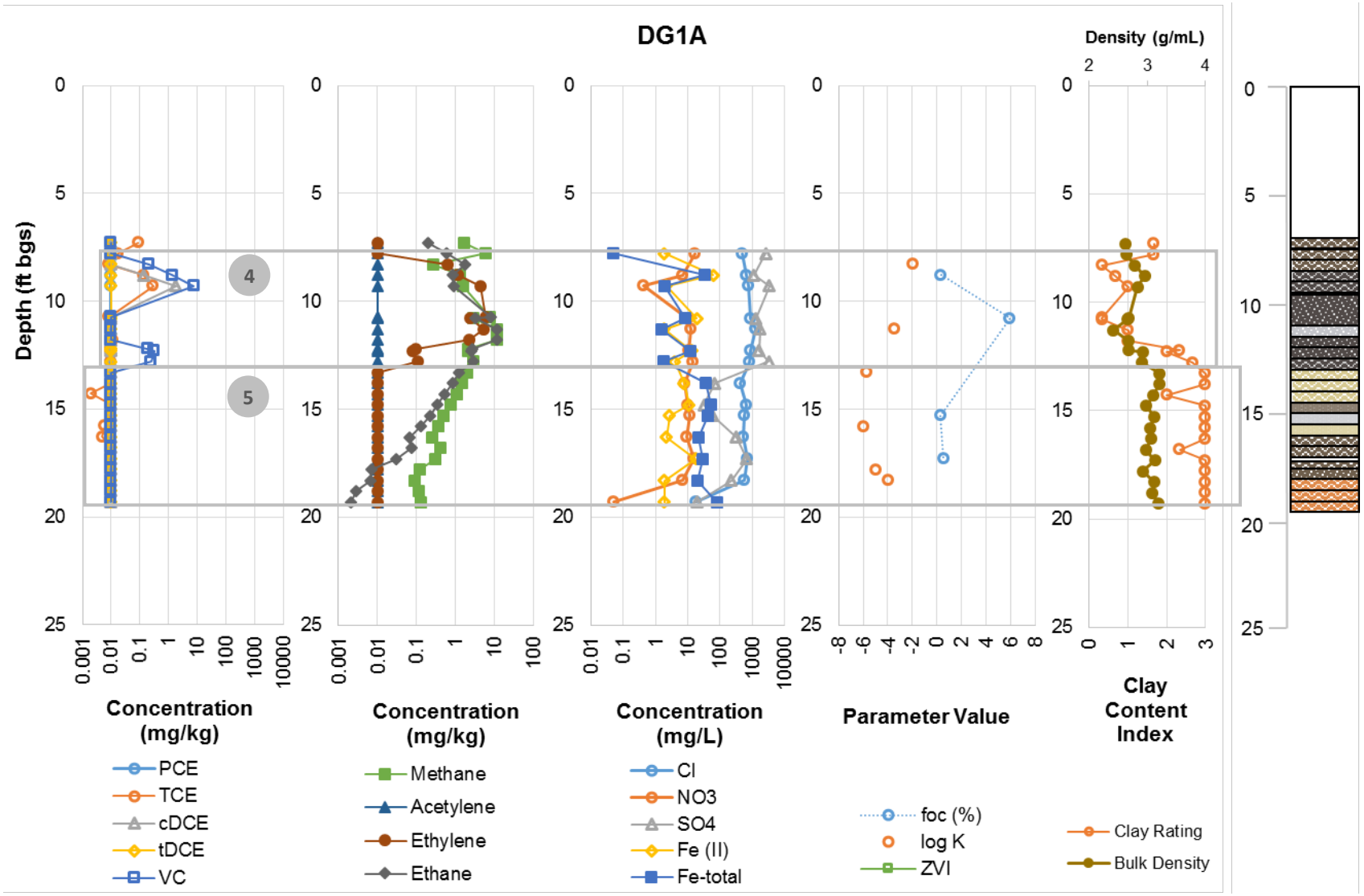

Figure 43c. Parallel Data Plots for Downgradient Location DG1A.

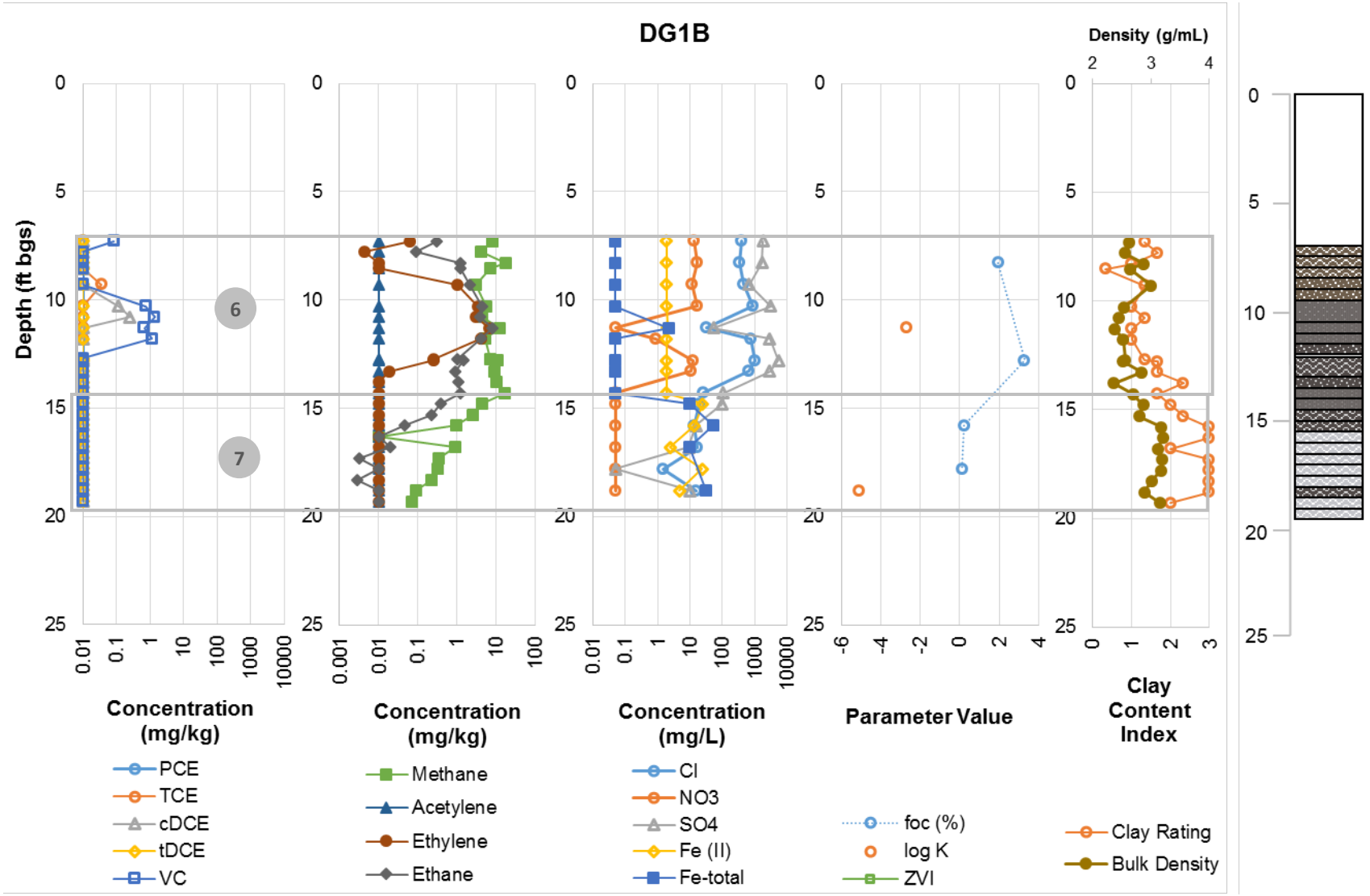

Figure 43d. Parallel Data Plots for Downgradient Location DG1B.

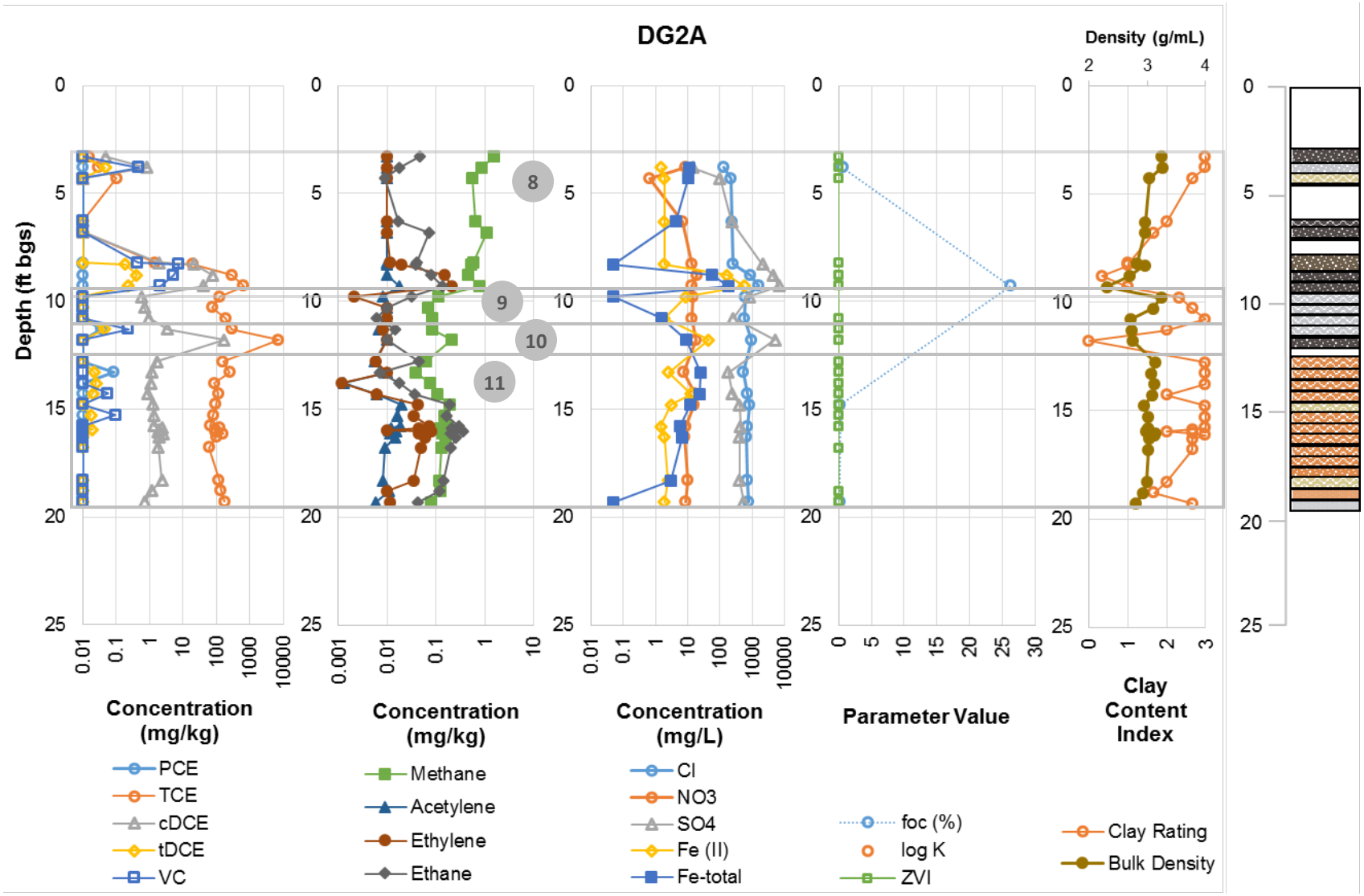

Figure 43e. Parallel Data Plots for Downgradient Location DG2A.

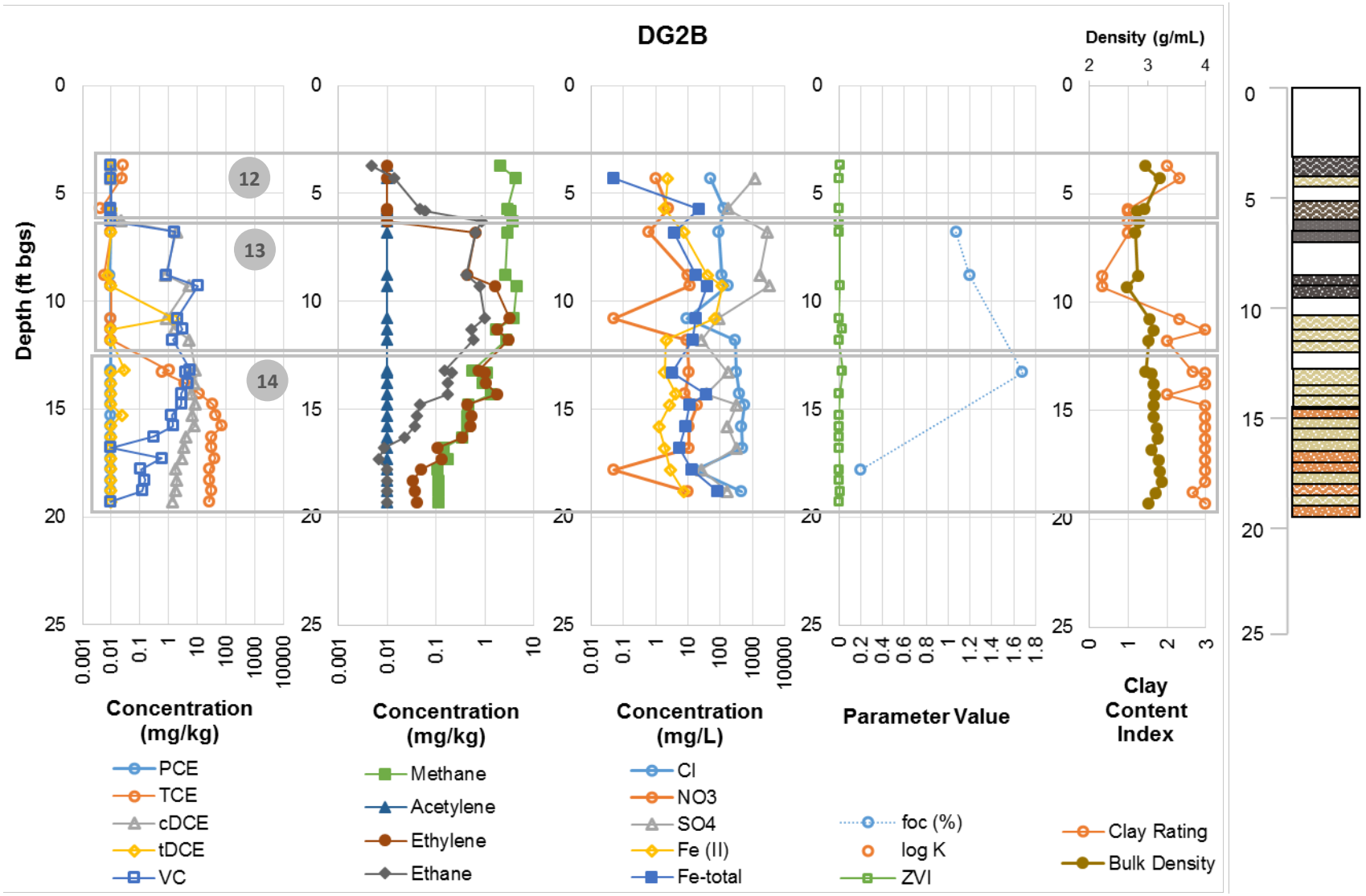

Figure 43f. Parallel Data Plots for Downgradient Location DG2B.

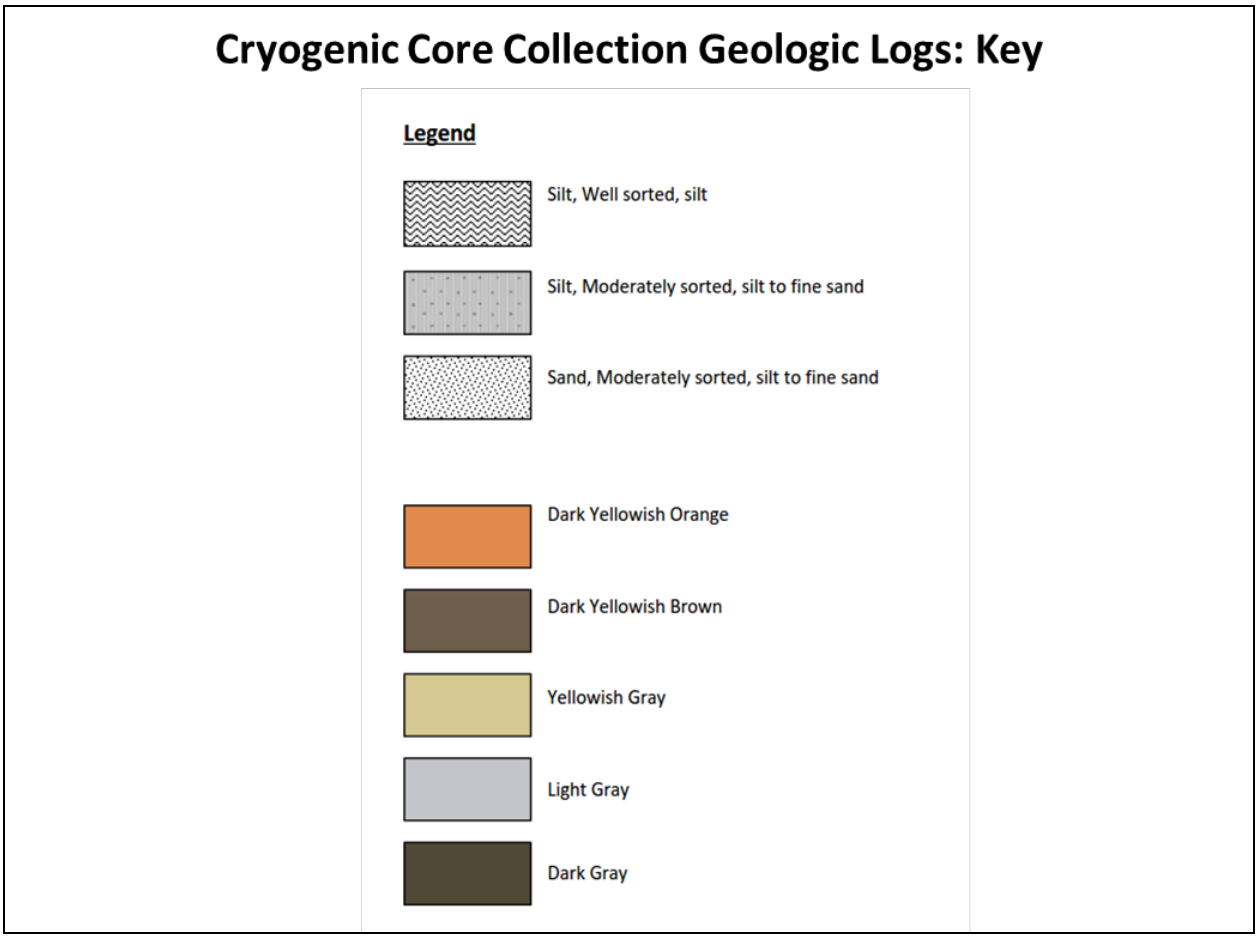

Figure 43g. Key for Geologic Logs.

SA1: *a source-area C_3-sampling location that was mixed with bentonite and 1% ZVI (weight basis). This location is in the western portion of the source area that contained relatively low concentrations of TCE (1 to 10 mg/L) prior to remediation. Recent groundwater data in adjacent monitoring well MW07 indicate TCE, cDCE, and VC concentrations of 0.027, 0.013, and 0.002 mg/L, respectively.*

1. Conditions are largely homogeneous across the mixed-soil depth interval. The Clay Content Index is at or near the maximum value (3.0), which is consistent with a zone mixed with bentonite. Low levels (<0.3 mg/kg) of TCE and *c*DCE persist over much of the vertical interval. Ethylene is below detection limits over the entire mixed interval; ethane is present at very low levels (<0.1 mg/kg), which tend to increase with depth. Overall, the lack of TCE degradation products suggests that active current TCE degradation at this location is minimal. Elevated chloride concentrations (150 to 240 mg/kg) are noted, providing evidence of past TCE degradation.

2. Beneath the mixed-soil depth (>18 ft bgs), concentration profiles for several analytes indicate diffusion is occurring within the underlying low-*k* clay. The "shark fin" shaped concentration profiles suggest back diffusion of contaminant mass out of the underlying clay into the treated soils may be occurring. In the case of a ZVI-mixed soil zone, back diffusion is not likely to cause concentration rebound, due to the presence of ZVI and reduced permeability within the mixed depth interval. Both VC and ethylene are below detection limits; ethane is present at concentrations near detection limits (<0.03 mg/kg). The presence of *c*DCE is noted, but may be related to the former source area, as opposed to current degradation of TCE within this low-*k* interval. Elevated sulfate within this interval (150 to 720 mg/L) may interfere with TCE biodegradation.

SA2: *a source area C_3-sampling location that was mixed with bentonite and approximately 3% ZVI (weight basis). Pre-mixing concentrations in nearby locations (up to 1500 mg/L in groundwater and up to 510 mg/kg in soil) suggested that TCE DNAPL may have been present in this area prior to soil mixing. Groundwater data from nearby monitoring well MW08 (see Appendix C) suggest TCE has been reduced by greater than 5 orders of magnitude in this area.*

3. Concentrations for most analytes are generally consistent over the mixed-soil depth interval. TCE and *c*DCE are present over much of the column, but at concentration ranges (non-detect to 0.2 mg/kg for TCE and non-detect to 0.9 mg/kg for *c*DCE,) that are substantially reduced from those present prior to soil mixing. Ethylene and ethane are both present over much of the depth interval, with elevated concentrations (up to 1.4 and 0.7 mg/kg for ethylene and ethane, respectively) occurring at 12 to 14 ft bgs; these data suggest that active TCE degradation is occurring, although very little of the TCE originally present in the area remains. Elevated chloride concentrations (1100 to 3300 mg/L) suggest a large quantity of chlorinated ethylenes have been degraded near this location; this is consistent with the observation of DNAPL formerly existing in the area. The clay content is highly variable, which is surprising in a soil area that was mixed with bentonite; the variability in this case may be attributed to unusual geochemical conditions resulting from soil mixing with 3% ZVI.

DG1A: *a downgradient C_3-sampling location that is near the mixed-soil zone and is part of transect DG1, which is oriented to the southeast toward monitoring well MW10.*

4. The Clay Content Index and geologic log suggest this depth interval is primarily transmissive, and transitions into low-*k* near the bottom of the interval. Mildly elevated concentrations of TCE, *c*DCE, and VC are present in a relatively narrow band (8 to 10 ft bgs) within this depth interval; maximum values for TCE, *c*DCE, and VC are 0.3, 1.8, and 7.5 mg/kg, respectively. Ethylene and ethane are also present, and tend to peak near the mid-point of the depth interval (maximum concentrations are 5.9 and 8.0 mg/kg for ethylene and ethane, respectively). A general trend is apparent, in which degradation products span a slightly wider depth interval than parent compounds. The presence of TCE degradation products suggest that active degradation of chlorinated ethylenes is occurring.

Near the bottom of this depth interval (i.e., > 12 ft bgs), TCE and cDCE are below detection limits, but a band of VC is present (up to 0.2 mg/kg). Minor concentration decreases with depth are observed for methane and ethane, but a major decrease occurs for ethylene. This suggests that active degradation of ethylene is occurring, which is a possible source of the ethane.

5. The Clay Content Index and geologic logs suggest that this is a low-*k* interval. TCE, *c*DCE, and VC are not detected in this interval. Methane and ethane are present, but concentrations decline exponentially versus depth; the concentration-versus-depth profiles for methane and ethane suggest diffusive transport. Ethylene is not detected.

DG1B: *a downgradient C_3-sampling location that is part of transect DG1, and is located near monitoring well MW10. Groundwater data from MW10 suggest that low levels of TCE and related products (<0.001 mg/L) are present in the vicinity.*

6. The low Clay Content Index and geologic log suggest this depth interval is primarily transmissive, but transitions to low-*k* near the bottom. The soil f_{oc} is relatively high (>2%). Products of TCE degradation, including *c*DCE, VC, ethylene, and ethane, reach peak values near the mid-point of this depth interval (10 to 12 ft bgs) and decline near the upper and lower boundaries. Relatively steep concentration-versus depth gradients are noted for VC and ethylene, whereas the ethane concentration gradient is more gradual. This suggests active biological degradation of VC and ethylene is occurring, with ethane formed as an end product. TCE is detected in only one sample, and that at a very low concentration (0.03 mg/kg). The lack of TCE presence in this interval, coupled with peak concentration of degradation products occurring in the transmissive zone, suggest TCE degradation may occur upgradient of this location.

7. The Clay Content Index and geologic logs suggest that this is a low-*k* interval. The soil f_{oc} is lower in the clay interval than in the overlying transmissive zone. TCE, *c*DCE, and VC are not detected in this interval. Methane and ethane are present, but concentrations decline exponentially versus depth; the concentration-versus-depth profiles for methane and ethane suggest diffusive transport is occurring. Ethylene is not detected.

DG2A: *a downgradient C_3-sampling location that is near the mixed-soil zone and is part of transect DG2, which is oriented to the northeast toward monitoring well MW02. Although this location was not included in the mixed-soil zone, the upper portion of the location may have been affected by excavation activities associated with soil mixing.*

8. The low Clay Content Index and geologic log suggest this is a transmissive depth interval, particularly near the bottom (8 to 9 ft bgs). The soil f_{oc} is extremely high (>25%) at 9 ft bgs, which is consistent with visual observation of the sample, which contained a weathered woody material. Elevated levels of TCE, *c*DCE, and VC occur in this depth interval (maximum values for TCE, *c*DCE, and VC were 670, 80, and 7.5 mg/kg, respectively). Ethylene, ethane, and acetylene are also detected. Detection of acetylene is unique to DG2A, and is considered evidence of abiotic degradation of TCE. Abiotic degradation may result from ZVI presence in the upgradient mixed-soil zone.

In a narrow band at the bottom portion of this interval, TCE concentrations change rapidly, increasing by four orders of magnitude over a depth interval of approximately 2 ft. Concentrations of *c*DCE and VC also increase by multiple orders of magnitude over this same depth range. Peak values are observed for several analytes (i.e., TCE, *c*DCE, VC, Fe(II), chloride, and sulfate) at a depth of 9 ft bgs, which corresponds with a minimal value for the Clay Content Index; this suggests a highly transmissive zone is present, possibly over a narrow depth interval. The buried wood observed at this location may account for high transmissivity, via preferential flow paths.

9. The geologic log and Clay Content Index suggest this is a low-*k* interval, forming a sharp contrast with the transmissive zones occurring above and below this interval. Concentrations of TCE, *c*DCE, and VC all decline in this interval, as compared to the concentration peaks observed in the adjacent transmissive zones. TCE remains elevated at concentrations greater than 100 mg/kg, *c*DCE declines to about 1 mg/L, and VC decreases to concentrations below detection limits.

10. This zone consists of an apparently narrow interval with a low Clay Content Index (transmissive), sandwiched between layers of a high Clay Content Index (low-*k*). A spike in TCE, *c*DCE, and VC concentrations corresponds with this apparent transmissive zone at 12 ft bgs. The TCE and *c*DCE concentrations (7300 and 170mg/kg, respectively) are higher in this depth interval than those observed anywhere else on site. Ethane and ethylene are detected within this interval, but at minimal concentrations (< 0.4 mg/kg).

11. This interval corresponds with the clay aquitard underlying Site 17. The Clay Content Index and geologic log suggest high clay content, in general, with possible interbedded zones of lesser clay content occurring. The TCE and *c*DCE concentration profiles indicate consistent concentrations through this interval (concentrations for TCE range from 90 to 180 mg/kg; concentrations for *c*DCE range from 0.7 to 2.6 mg/kg). The consistent concentrations may be due to the close proximity to the former source zone; this location is close to the portion of the former source zone that likely contained DNAPL. Ethane, ethylene, and acetylene are detected within this interval (maximum concentrations for ethane, ethylene, and acetylene are 0.35, 0.08, and 0.02 mg/kg, respectively). The presence of acetylene and ethylene suggests that degradation may be occurring within this interval.

DG2B: *a downgradient C_3-sampling location that is part of transect DG2, and is located near monitoring well MW02. In MW02, transient increases in TCE degradation products (cDCE and VC) were observed approximately 1 to 2 years after soil mixing was completed; these compounds subsequently decreased, prior to cryogenic coring.*

12. The upper portion of DG2B is characterized by concentrations that are near or below detection limits for the analytes of primary interest (TCE, *c*DCE, VC, ethane, and ethylene). At a depth of approximately 6 ft bgs, concentrations for each of these analytes (except TCE) increase by one or more orders of magnitude. Shallow soils and groundwater across much of Site 17 appear to be relatively unaffected by TCE and related products.

13. At depths of 6 to 12 ft bgs, TCE concentrations remain at or near detection limits. Elevated concentrations of *c*DCE (up to 5.2 mg/kg) and VC (up to 10.8 mg/kg) are observed. Similarly, ethane and ethylene concentrations fluctuate within a relatively small range over this interval (ethylene ranged from 0.6 to 3.1 mg/kg; ethane ranged from 0.1 to 1.0 mg/kg). Clay Content Index values suggest that low to moderately high clay is present over the interval.

14. The Clay Content Index and geologic logs suggest that this is a low-*k* interval. The soil f_{oc} is lower in the clay interval than in the overlying transmissive zone. TCE, *c*DCE, and VC are detected throughout this interval, although trends are slightly different for the different compounds. TCE concentrations increase rapidly, by about four orders of magnitude (from non-detect to approximately 40 mg/kg), in the upper 3 ft of this interval; in the lower 5 ft of this interval TCE concentrations remain fairly consistent (27 to 75 mg/kg). Concentrations of *c*DCE and VC undergo gradual decreases with depth, with VC declining at a steeper gradient than *c*DCE. Ethylene concentrations decline with depth, but persist at approximately 0.04 mg/kg in deeper samples; the declining concentration with depth suggests that diffusion may be sustaining elevated concentrations in shallower samples, but that chlorinated ethylene degradation may be occurring within this low-*k* zone.

6.1.2 Comparison of High-Resolution C_3 Data to Temporal Groundwater Data

This subsection presents a direct comparison of groundwater data, generated via routine sampling of monitoring wells, to the high-resolution C_3 data. The purpose of this evaluation is to support the performance objective (i.e., assessment of long-term remediation impacts using both existing and high-resolution data) by tying the high-resolution data into the existing groundwater data set. The soil-core locations were selected, in part, based on proximity to existing monitoring wells. For this comparison, groundwater data from adjacent monitoring wells, based on sampling conducted at a similar time to cryogenic coring, is presented on a single plot with the depth-resolved C_3 data.

This comparison of monitoring-well to C_3 data provides useful insights, but discretion should be employed when interpreting these results. In particular, water flow from heterogeneous porous media into a monitoring well is a complicated process, such that monitoring-well groundwater data may not directly represent depth-resolved total-concentration data. For example, monitoring wells may be affected by narrow bands of high groundwater flow, or transport (via diffusion or advection) of contaminant mass from outside the screened interval. Also, note that the soil-core locations are typically 3 to 5 feet from the monitoring well, and conditions may change over this distance. While these considerations should be taken into account, substantial value can be derived from this comparison, as described herein.

Data are shown for chlorinated ethylenes (TCE, *c*DCE, and VC) and gaseous organics (methane, ethane, and ethylene). The two source-area soil-core location/monitoring well pairs included in the analysis are as follows:

- SA1 and MW07 (Figure 44)

- SA2 and MW08 (Figure 45)

The two downgradient soil-core location/monitoring well pairs included in the analysis are as follows:

- DG1B and MW10 (Figure 46)
- DG2B and MW02 (Figure 47)

The associated monitoring well, and the screened interval of the associated well, is indicated on each of Figure 44 to Figure 47. Groundwater data is shown for April 2016, the monitoring event closest to the time of cryogenic coring (June 2016). Complete groundwater data versus time, for each of the monitoring wells included in Figure 44 to Figure 47, is shown in Appendix H.

For this analysis, C_3-generated concentration data, which was generated on a total-sample basis (mg/kg), was converted to a pore-water equivalent (units of mg/L) using the following conversion:

$$C_p = C_{total} \frac{\rho_w (1 + 1/w)}{(1 + K_d \rho_w / w)}$$

where C_p (mg/L) is the pore-water equivalent concentration, C_{total} (mg/kg) is the total concentration on a wet soil basis, ρ_w (g/mL) is the density of water, w (g/g) is the gravimetric water content and K_d (L/kg) is soil/water partition coefficient. The value of K_d was calculated as the product of f_{oc} and the organic carbon partition coefficient, K_{oc} (L/kg). No soil-phase partitioning was assumed for the gaseous products (i.e., $K_d = 0$).

In both of the source-area soil-core location/monitoring well pairs (see Figure 44 and Figure 45), the C_3 data within the screened interval are generally agreeable with groundwater well data. Low groundwater concentrations of TCE, *c*DCE, and VC ($\leq$ 0.027 mg/L) correspond with the range of C_3 data within the well-screen depth interval. A minor exception occurs in MW08, in which TCE concentration (0.0012 mg/L) is lower than the TCE range observed in C_3 data (0.006 to 0.1 mg/L); the difference may be attributed to the immobility of TCE remaining in the ZVI-mixed soil zone.

The gaseous organic data also suggests general agreement between monitoring well and C_3 data. Elevated methane (>10 mg/L) is observed in both of the source-area monitoring wells, which is within range of the C_3 methane data over the screened interval. The ethane concentration in groundwater is lower in MW07 (0.08 mg/L) than in MW08 (2.2 mg/L), which is consistent with C_3 data. Similarly, ethylene was not detected in MW07 (<0.0003 mg/L) or in C_3 data from location SA1 (although detection limits were higher for C_3 data than for groundwater data); ethylene was detected in groundwater sampled from MW08 (1.3 mg/L), which was within the range of C_3 data from the adjacent location SA2.

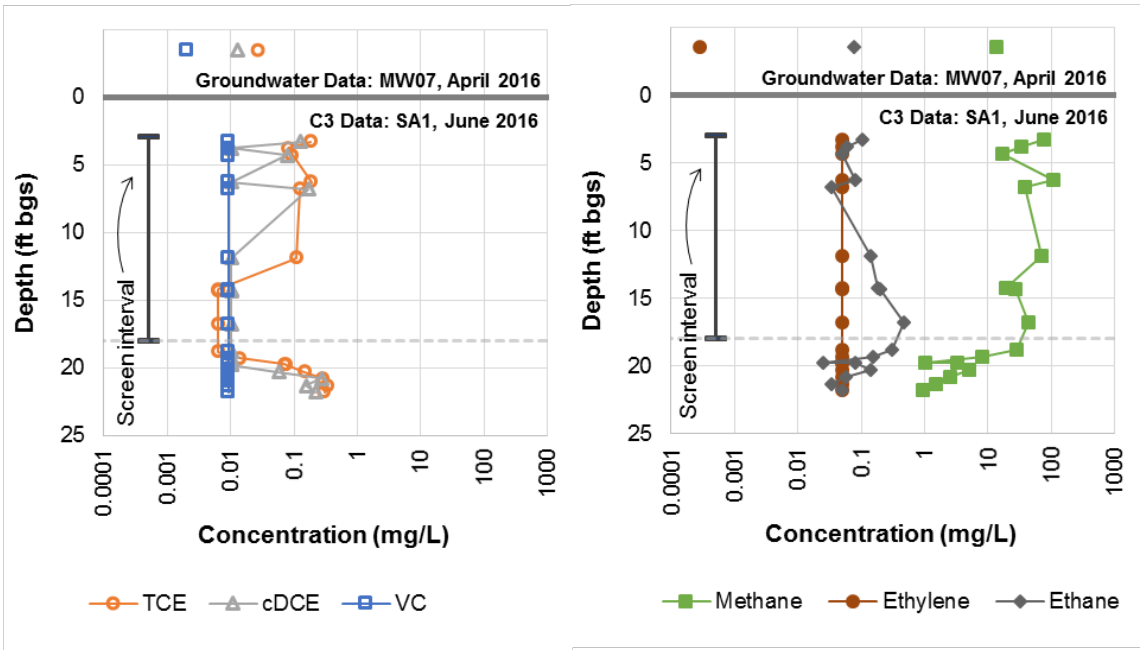

Figure 44. Comparison of C_3 Data to Monitoring-well Groundwater Data: SA1 and MW07.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

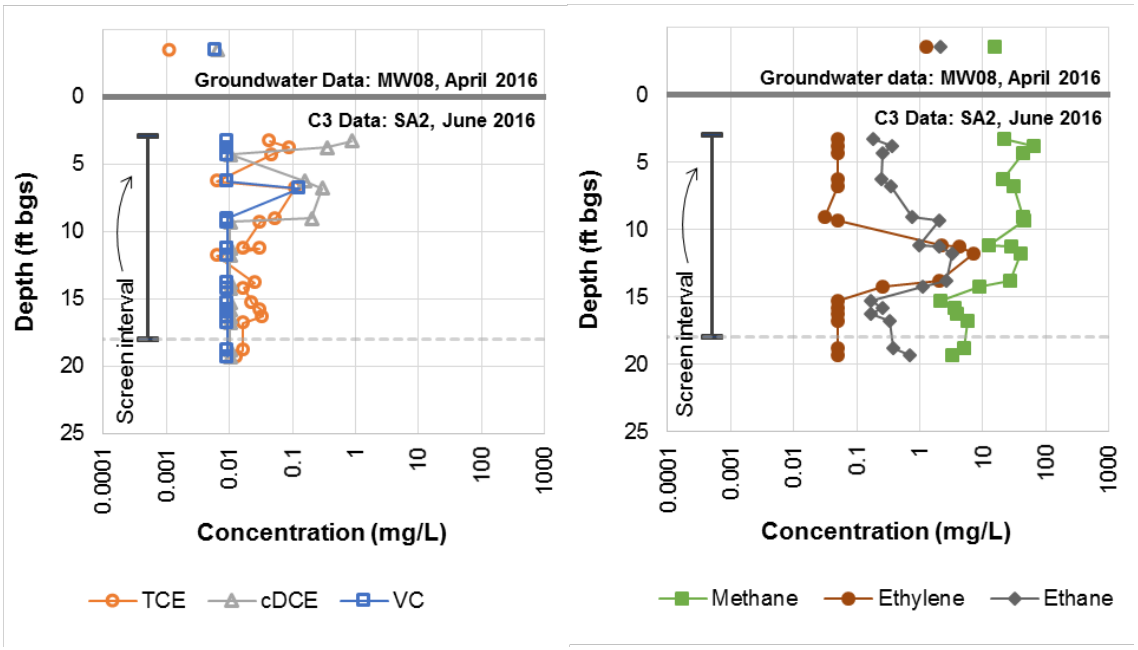

Figure 45. Comparison of C_3 Data to Monitoring-well Groundwater Data: SA2 and MW08.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

In the downgradient soil-core location/monitoring well pairs (see Figure 46 and Figure 47), the C_3 data are generally agreeable with monitoring-well groundwater data, but more exceptions are noted than were apparent in the source-area comparison. For both chlorinated and gaseous organics, a general observation is that higher concentrations are apparent in the C_3 data, over the screened depth intervals, than are apparent in the groundwater monitoring wells. This likely results from the fact that groundwater monitoring-well data reflects a vertically integrated sample; low- and high-concentration depth intervals are effectively blended via sampling of long-screen monitoring wells. Also, C_3 data accounts for contaminant mass in all phases, including sorbed, which may be excluded from groundwater monitoring well data; a more detailed discussion is provided below.

Concentrations of chlorinated ethylenes were detected in C_3 data from DG1B at concentrations up to 0.45 mg/kg (TCE), 0.36 mg/kg (cDCE), and 1.4 mg/kg (VC). However, detection occurred only over a narrow depth interval. In the adjacent monitoring well MW10, the chlorinated ethylenes were either not detected (*c*DCE and VC) or were only detected at very low levels (TCE; "J-flag" estimated at 0.0008 mg/L). Thus, at this location, the band of higher C_3 data is not suggested by the groundwater data from the adjacent monitoring well, MW10.

The second downgradient comparison, which includes soil-core location DG2B and monitoring well MW02 (Figure 47), provides an insightful case study; therefore, additional detail is included for this comparison. In C_3 data from location DG2B, TCE is present at low concentrations (approximately 0.002 to 0.006 mg/L) over the screened interval for MW02. Below the screened interval, TCE concentrations increase by approximately three orders of magnitude over a depth interval of less than 5 ft. In adjacent monitoring well MW02, TCE was not detected (<0.0025 mg/L); this result is consistent with the C_3-data concentration range within the screened interval, but provides no indication of the high concentration present a few feet below the screened interval. Concentration trends for *c*DCE and VC were different from that observed for TCE. Both *c*DCE and VC were present at low levels (<0.2 mg/L) at the top of the screened interval, and abruptly increased by about two orders of magnitude within the screened interval. Concentration data in MW02 (0.13 and 0.56 mg/L for *c*DCE and VC, respectively) were lower than peak concentration values observed within the screened interval, suggesting that groundwater data represents a blending of high- and low-concentration strata.

In both of the downgradient soil-core locations, methane concentrations are relatively consistent over the screened interval, and monitoring well data is within the range of C_3 data. Ethane and ethylene are both more variable, with concentrations varying by two (or more) orders of magnitude over some portion of the screened interval. As a result, the groundwater concentrations of ethane and ethylene are lower than the maximum values by approximately 0.5 to 2 orders of magnitude; a possible explanation involves in-well mixing of water from low- and high-concentration strata.

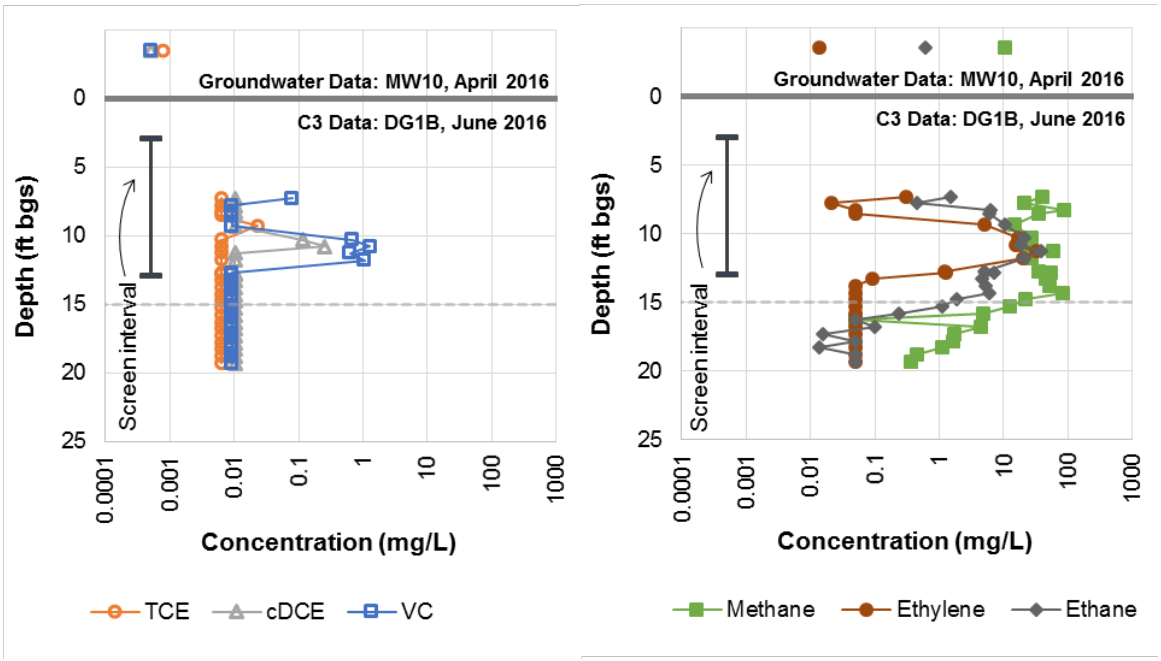

Figure 46. Comparison of C_3 data to Monitoring-well Groundwater Data: DG1B and MW10.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

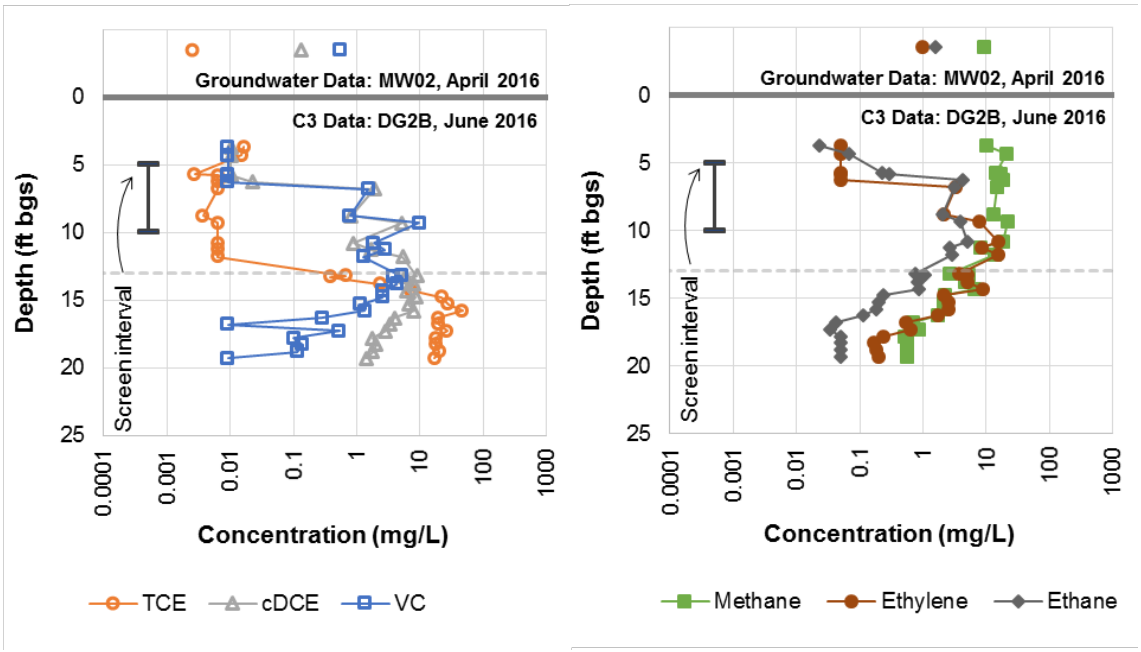

Figure 47. Comparison of C3 data to Monitoring-well Groundwater Data: DG2B and MW02.

Note: the dashed line indicates the approximate geologic transition between the underlying clay aquitard (low-k) and overlying zone, comprising ZVI-Clay mixed soils (low-k) for "SA" locations or interbedded sand/silts (transmissive) for "DG" locations.

The general consistency (with exceptions noted) between C_3 data and data from adjacent groundwater monitoring wells indicates that the two data sets can provide a symbiotic relationship that enhances the value of both. When analyzed together, the C_3 data provide an extra dimension to data from a groundwater monitoring well. When evaluated independently, monitoring well data provide little information about the vertical distribution of high- and low-concentration depth intervals, and no information about contaminant presence outside of the screened interval. C_3 can complement monitoring wells data by addressing these data gaps and providing context for evaluating trends apparent in monitoring well time-series data. Similarly, cryogenic coring is probably not a cost-effective method for collecting data over time, but groundwater monitoring wells can supplement C_3 data to evaluate temporal trends.

6.2 MIXED-SOIL ZONE BIOGEOCHEMICAL CONDITIONS

This performance objective is intended to evaluate the effectiveness of the remediation in eliminating the treated-soil zone as a long-term source of groundwater contamination. To evaluate this performance objective, existing data were analyzed and supplemented with high-resolution data to address the potential for continued degradation in the treated source zone.

6.2.1 Performance Assessment Based on Existing Data

Existing performance data suggests that the remediation was highly effective in terms of contaminant mass reduction. Peak groundwater TCE concentrations declined by several orders of magnitude, including a decline by greater than five orders of magnitude in the area of monitoring well MW08 (which was installed about one year after soil mixing remediation was complete), when coupled with data from direct push location DP70 (which provided data from a similar location, before remediation and through the first year after soil mixing was complete). However, the data suggest that a relatively small quantity of TCE and *c*DCE remains within the treated source zone. In groundwater data collected in April 2016, remaining groundwater TCE concentrations were 0.027 and 0.001 mg/L in MW07 and MW08, respectively (the MCL for TCE is 0.005 mg/L).

6.2.2 Performance Assessment Based on C_3 Data

High-resolution data generated in this project, for parameters that are relevant to this performance objective, are presented on parallel-data plots for the treated-soil zone locations (Figure 43a and Figure 43b for locations SA1 and SA2, respectively). The parallel-data plots indicate that conditions are reasonably homogeneous within the treated soil zone, as expected following soil mixing. Remaining TCE and *c*DCE occurs primarily in the shallower soils (depth <12 ft bgs). Ethylene is not detected in SA1 but is detected in SA2, which suggests that ongoing TCE degradation occurs within portions of the treated source zone. Elevated chloride concentrations in both locations are consistent with prior degradation of large quantities of chlorinated ethylenes; chloride concentrations are typically higher in SA2, which formerly contained DNAPL, than in SA1.

ZVI content analysis suggests that iron remains in the mixed soil zone, and that some iron remains in the reactive zero-valent oxidation state. The reactivity studies confirmed that remaining ZVI was potentially reactive. The reactivity studies, which were not intended to quantify reaction rates, indicated that soil samples from both source-area locations were able to achieve degradation of TCE, as confirmed by formation of degradation products. The soils from SA1, which was mixed with a target amount of 1% ZVI, appeared to be more reactive than soils from SA2, for which 3% ZVI was the target amount. The higher contaminant concentration, including possible presence of DNAPL, might have resulted in consumption of ZVI in the SA2 area; however, ongoing potential reactivity was observed in both locations.

Based on observations of reduced contaminant concentrations, lack of heterogeneity in the mixed-soil zone, and ongoing reactivity of ZVI, there appears to be little probability of a rebound occurring in the treated-soil zone.

6.3 DOWNGRADIENT TREATMENT PROCESSES AND PERFORMANCE

This performance objective involves an evaluation of downgradient treatment processes and performance to assess the influence of the source-zone remediation. To evaluate this performance objective, transect-data plots are shown for transects DG1 and DG2 in Figure 48 and Figure 49, respectively. Vertical concentration profiles within each soil-core location were discussed in detail in Section 6.1; this section focuses on spatial variability between locations.

6.3.1 Transect DG1

In transect DG1, the downgradient locations do not show a strong relationship with current source-zone conditions. Contamination is present over a relatively narrow band in the downgradient locations (8 to 10 ft bgs in DG1A and 10 to 12 ft bgs in DG2B), whereas remaining contaminant mass appears to be spread over a wider depth interval (4 to 12 ft bgs in SA1) in the mixed-soil zone. Furthermore, *c*DCE and VC were below detection limits in source zone locations (SA1 and SA2), but were present in downgradient locations at concentrations up to 1.8 and 7.5 mg/kg, respectively. The lack of strong connectivity between the treated-soil zone and downgradient locations is consistent with the CSM, in which groundwater flow through the treated-soil zone is substantially reduced after soil mixing.

In the downgradient locations comprising transect DG1, a band of TCE degradation products appears to be present in a relatively narrow depth interval in the upper transmissive zone. In general, each degradation product tends to spread over a slightly wider depth interval than its related parent compound. For example, ethylene spans a greater depth interval than VC, which in turn spans a greater depth interval than *c*DCE. This trend remains apparent at locations farther downgradient from the former source. The contaminated interval is slightly deeper in the farthest-downgradient location. This observation is consistent with the geologic data and Clay Content Index presented in Figure 43c and Figure 43d, which suggest that the transition to the underlying clay also occurs about 2 ft deeper in DG1B than in DG1A.

In the underlying low-*k* zone, chlorinated ethylenes are generally below detection limits in both of the DG1 downgradient locations. For gaseous products, ethane is present but ethylene is not.

The ethane concentration appears to decline exponentially with depth, which suggests vertical diffusive transport. Furthermore, the presence of ethane, without local presence of ethylene, indicates that ethylene is degraded relatively quickly after formation, whereas ethane persists. This is consistent with ethane being an end product of chlorinated ethylene degradation.

Overall, the results in transect DG1 suggest that at that location, the chlorinated ethylene mass occurred almost exclusively in the transmissive zone. This suggests that soils in this transect have not been historically exposed to high contaminant concentrations, which would likely have resulted in diffusive transport into adjacent low-*k* zones. Aside from ethane, diffusion into the underlying low-*k* zone does not appear to be an important governing process in this transect. In addition, the results suggest that the modest chlorinated ethylene concentrations present in the transmissive zone are being actively degraded.

6.3.2 Transect DG2

In transect DG2, the concentration profiles observed in downgradient locations do not show a strong relationship with the former source area. As discussed in the previous subsection, this observation is consistent with the CSM.

The geology and Clay Content Index for downgradient locations in DG2 suggest a (slightly) higher degree of heterogeneity in the zone overlying the aquitard than in the DG1 locations (Figure 43c through Figure 43f). The chlorinated ethylene concentrations are substantially higher than those observed in DG1. Near the source area in transect DG2, elevated concentrations of TCE and *c*DCE are observed over much of the vertical profile, including transmissive and low-*k* zones. The presence of elevated concentrations in the transmissive zone, immediately downgradient of the treated-soil zone, suggest that the hydraulic shadow effect (Section 4.4.1) may be affecting areas immediately downgradient of the treated zone, resulting in very low rates of groundwater advection. Farther from the source area, concentrations in the transmissive zone are depleted but elevated concentrations are present in the low-*k* zone. The differing transmissive-zone concentrations suggest one of the following: (a) the location DG2B is in fact not hydraulically downgradient from DG2A, or (b) chlorinated ethylene mass in the transmissive zone is depleted between the two locations.

Within the low-k zone:

- TCE concentrations are similar in magnitude in DG2A (approximately 5 ft from the treated-soil zone) and DG2B (approximately 60 ft from the treated-soil zone);
- *c*DCE concentrations are similar in magnitude in DG2A and DG2B ;
- VC concentrations are 1 to 2 orders of magnitude higher in DG2B, which is farther from the treated soil zone;
- Ethylene concentrations are 1 to 2 orders of magnitude higher in DG2B, which is farther from the treated soil zone; and
- Acetylene is only detected in DG2A, near the source area.

Acetylene is detected near the treated-soil zone, but is non-detect downgradient. Thus, evidence of abiotic degradation is limited to the area nearest the ZVI-mixed soil zone.

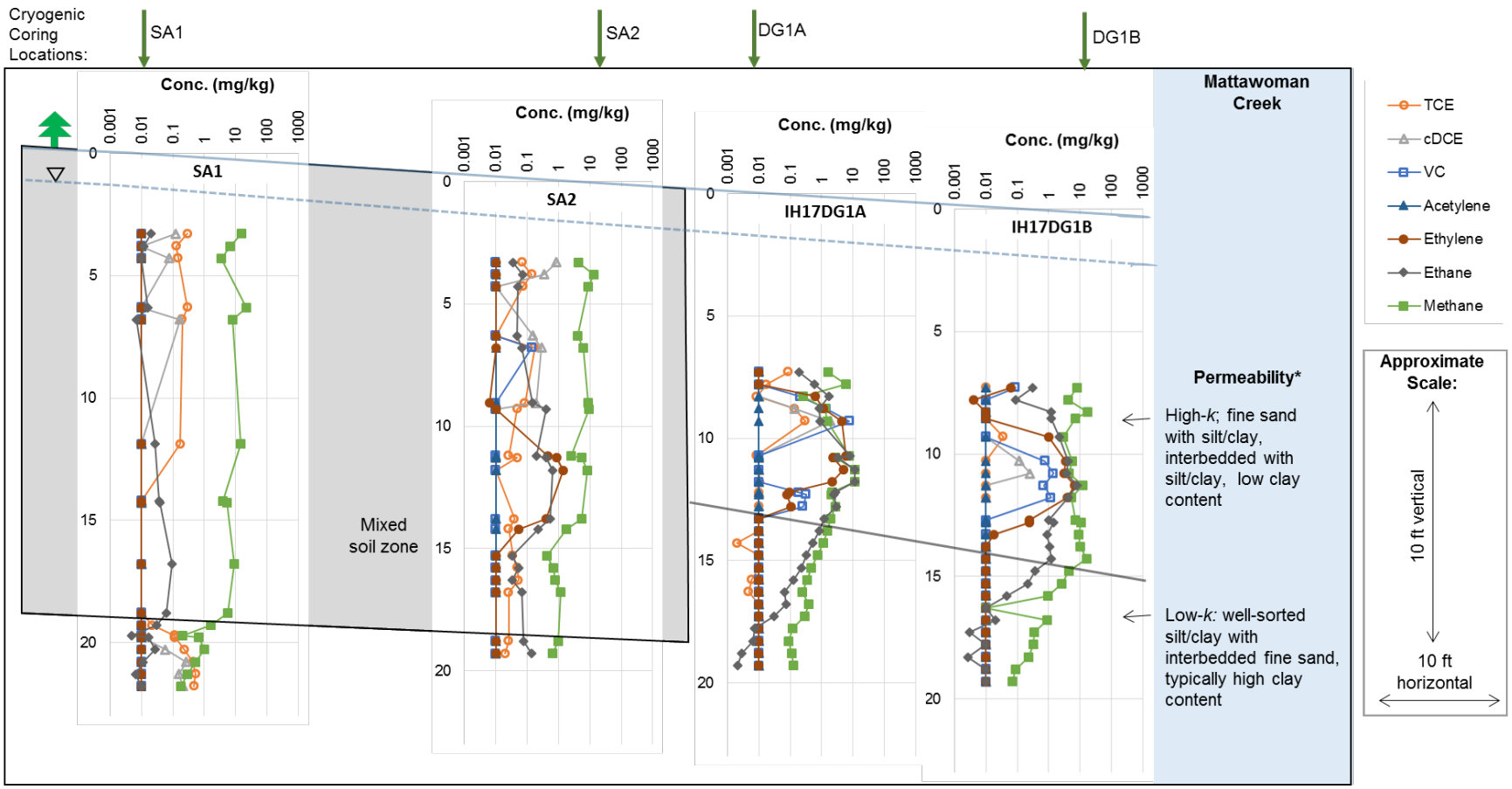

Figure 48. Cross-section of TCE and Degradation Product Data for Source-area and Transect DG1 Cryogenic-coring Locations.

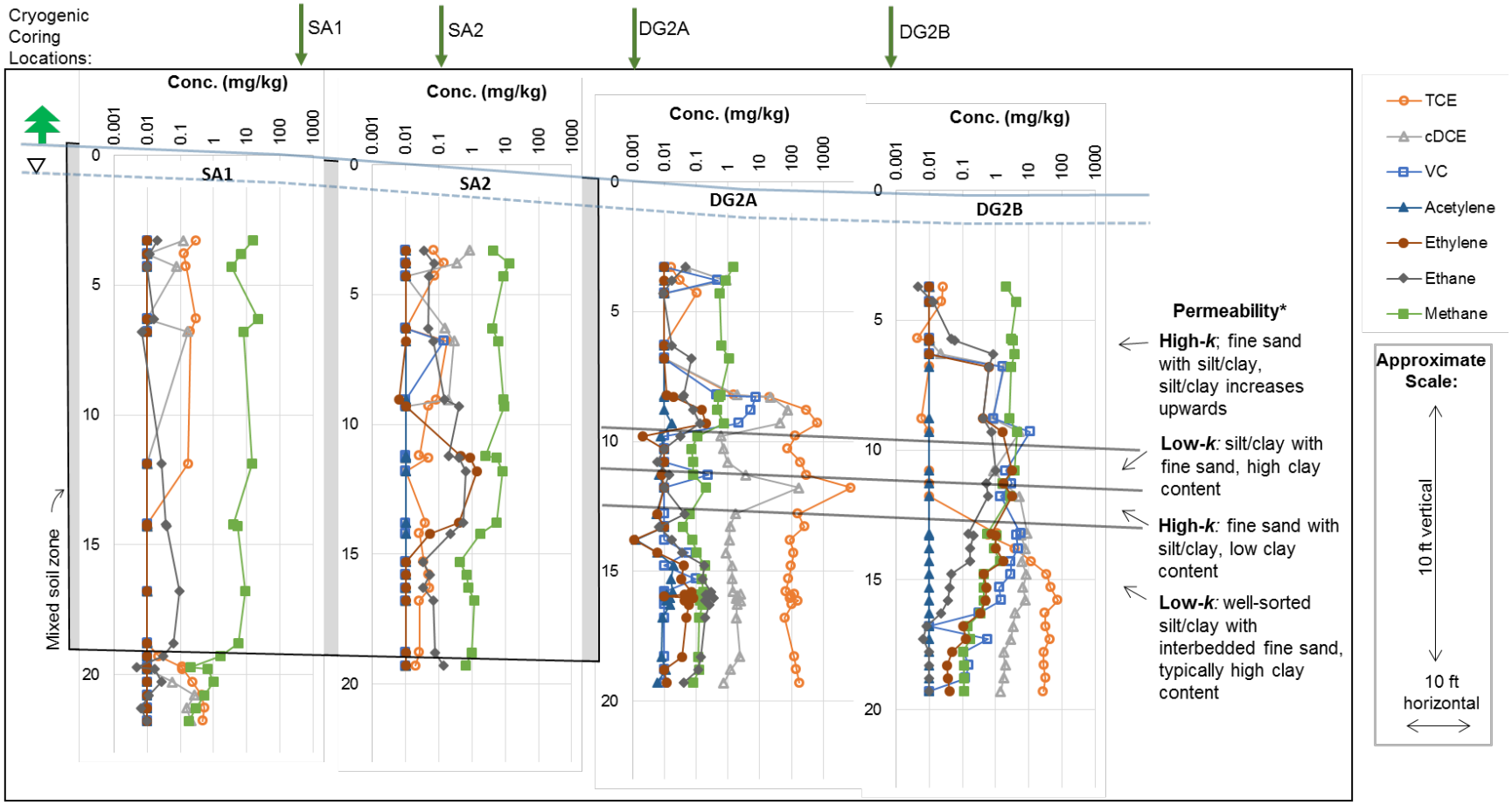

Figure 49. Cross-section of TCE and Degradation Product Data for Source-area and Transect DG2 Cryogenic-coring Locations.

6.4 CRYOGENIC CORING RECOVERY AND PRODUCTION RATE

6.4.1 Soil Core Recovery

This performance objective was included to evaluate the C_3 technology for the ability to provide near-perfect core recovery, as has been observed in some field applications. In accordance with this performance objective, core recovery of at least 90% is considered successful, and an explanation would be required for locations where core recovery was less than 90%. The calculated soil recovery values, calculated for each frozen-core section as the length of soil core divided by the target length (30 in.), are shown in Figure 50. Recovery of 90% or greater was achieved in 14 core sections of 39 total (36%). By comparison, recovery of less than 50% occurred in 13 core sections (33%). The recovery data shown in Figure 50 is divided into core sections collected from within the mixed-soil zone and those collected from downgradient locations. Most of the core sections with recovery of 90% or greater occurred outside of the mixed soil zone. Conversely, most of the core sections with less than 50% recovery occurred within the mixed-soil zone.

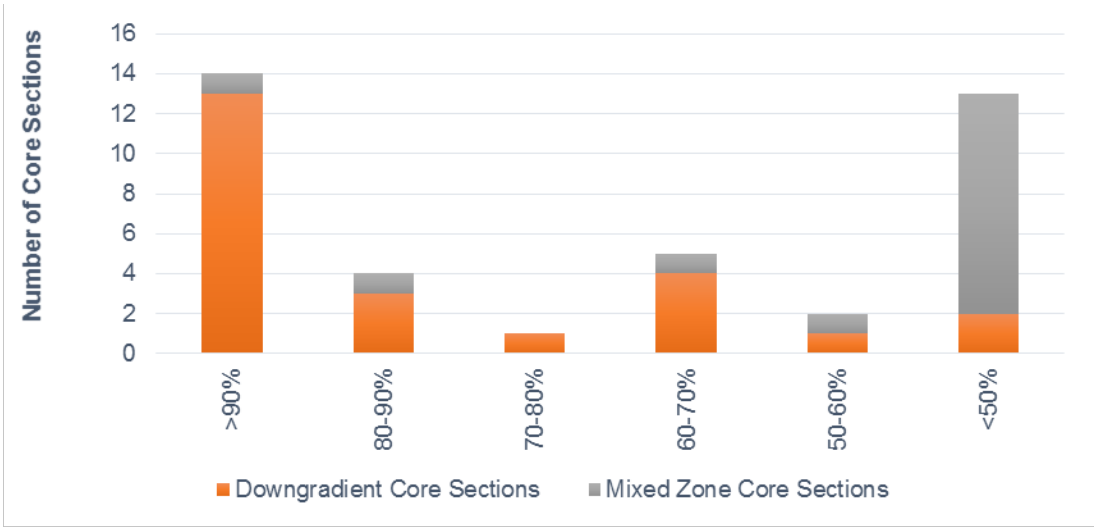

Figure 50. Soil Core Recovery Data, Separated by Mixed-zone and Downgradient Cryogenic Coring Locations.

During the cryogenic coring activities at Site 17, two primary factors were observed that limited core recovery. First, within the mixed soil zone, the soils were relatively soft and "squishy," a property that can be attributed to mixing of the soils with bentonite. Reduced load-bearing capacity of bentonite-mixed soils has been documented in a Master's Degree thesis (Vianna 2009). From this observation, we can infer that the soft mixed-zone soils were pushed out of the way of the advancing core sampler, rather than filling the tube as designed.

The second observation involves subsurface woody debris, which was encountered at depths of 8 to 12 ft bgs. This buried wood was originally present in the mixed-soil zone, but was excavated prior to soil mixing activities (CH2M 2013); the soil-mixing completion report described the excavated material as "logs and tree stumps." During cryogenic coring activities at Site 17, woody debris was encountered at each of the locations outside of the mixed zone.

The first location sampled outside of the mixed zone was DG2B; initially, little to no recovery occurred after a depth of about 5.5 ft bgs. To investigate the cause of the poor recovery, an auger was attached to the drill rig and was advanced into the subsurface, and the woody material was discovered. Subsequently, the location was moved about 3 ft to the southwest, the auger was used to advance past the layer of woody material, and core-collection was resumed. Wood was encountered at a depth of approximately 7 ft bgs at the next soil-core location (DG2A); the location was moved about 3 ft to the northeast for samples at depths greater than 7 ft bgs. For the remaining two locations (DG1A and DG1B), soils were initially augered to a depth of approximately 7 ft bgs to investigate for the presence of wood; wood was encountered at both locations. Thus, cryogenic coring began at a depth of 7 ft bgs at both locations in transect DG1.

In summary, although recovery of 90% or greater was not achieved in the majority of samples, this performance objective is considered to have been addressed, as explanations are available for core sections with <90% recovery. The primary issues that affected recovery included soft soils in the mixed-soil zone and woody debris in the downgradient locations. Neither of these issues is directly related to the C_3 procedure (i.e., the issues would remain if traditional soil-coring methods were being implemented). For future use of the technology in soft soils such as those encountered in the mixed soil zone (or similarly soft soils, such as sediments), development of a modified Shelby-tube type C_3 tool may be beneficial.

6.4.2 Field Sampling Production Rate

The goal was to meet or exceed the previous production rates of about 30 feet per day. Cryogenic coring activities at Site 17 were conducted over three days, from June 21 to 23, 2016 (plus mobilization and demobilization, which were completed on June 20 and June 24, respectively). A summary of daily collection activities is shown on Table 11. The average production rate was 33 ft/day, which is similar to the production rates obtained in recent C_3 projects.

Table 11. Daily Production Summary

Date	Sampled Locations	Daily Sampled Interval (ft)
6/21/2016	SA1 and SA2	37.5
6/22/2016	DG2A and DG2B	34.3
6/23/2016	DG1A and DG1B	25.0

Minor delays were encountered due to (a) coring equipment freezing downhole, (b) freezing or binding of the core sample in barrel, and (c) running out of LN in the vicinity of sampling. Downhole freezing of coring equipment may occur when LN is circulated too long. This issue was only encountered once at Site 17. Freezing of the core sample in the barrel was the cause of minor delays (typically <10 min); when this occurred, the sample was removed by circulating steam through the LN circulation system to remove ice buildup. On one occasion, the readily available LN supply was completely consumed, and the cryogenic coring activities had to stop while the support vehicle retrieved more LN from the staging area. This issue was addressed by bringing an extra LN dewar to each new location.

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7.0 COST ASSESSMENT

This project involved both the ZVI-Clay remediation technology and C_3 characterization. The former TCE source-zone was remediated using the ZVI-Clay Soil Mixing technology approximately four years prior to this project. Detailed cost-tracking data for the ZVI-Clay technology were not available; however, a detailed cost assessment of the ZVI-Clay Soil Mixing remediation technology has been published by Harkness and Konzuk (2014). A summary of this ZVI-Clay Soil Mixing cost assessment, adapted for the soil mixing application at Site 17, is presented herein (Section 7.1). Subsequently, a detailed cost analysis is presented for the C_3 characterization technology (Section 7.2), for which a detailed cost estimate has not yet been published.

7.1 ZVI-CLAY COST ASSESSMENT

The cost analysis presented herein is based on the analysis developed by Harkness and Konzuk (2014), adapted to Site 17. The approach employed by Harkness and Konzuk involved "detailed costing [of remediation technologies] for hypothetical template sites" comprising source areas impacted with TCE DNAPL. The analysis presented by Harkness and Konzuk compares ZVI-Clay Soil Mixing to alternative standard source-zone treatment technologies, including enhanced *in situ* bioremediation (EISB), *in situ* chemical oxidation (ISCO), thermal remediation, and excavation. The hypothetical site conditions evaluated included the following:

- A 1500 m^2 (1800 yd^3) footprint, with contamination present to a depth of 4.5 m (15 ft) bgs, for a treatment volume of 6750 m^3 (9000 yd^3).
- Heterogeneous geology with hydraulic conductivity values of 10^{-5} to 10^{-4} cm/sec.
- Contamination consisting primarily of TCE, with groundwater concentrations up to 500 mg/L.
- Low-DNAPL, base-case, and high-DNAPL scenarios (comprising total TCE masses of 1500 kg; 15,000 kg; and 60,000 kg, respectively).

7.1.1 ZVI-Clay Cost Model

The Harkness and Konzuk (2014) cost model for ZVI-Clay Soil Mixing was employed for this analysis, with select modifications employed to fit conditions at Site 17. Implementation of ZVI-Clay Soil Mixing is completed in a single treatment event, unlike injection-based technologies that may require multiple injections over several years. Thus, the only long-term costs associated with implementing the technology are those required for monitoring. The cost model presents only those costs associated with design and implementation (Table 12). For comparison, a cost model for excavation is also shown.

Table 12. ZVI-Clay Cost Model [1]

Cost Element	Item Description	Large site[2]				Small site[3]	
		ISCR	Excavation	Scalable?	Scale factor[4]	ISCR	Excavation
Design	Laboratory studies	$25,000	$5,000	No	1	$25,000	$5,000
	Detailed design, permitting, and reports	$75,000	$50,000	No	1	$75,000	$50,000
	Procurement	$11,000	$15,000	No	1	$11,000	$15,000
	Total Design	**$111,000**	**$70,000**			**$111,000**	**$70,000**
Implementation	Site preparation	$20,000	$10,000	Yes	0.14	$2,800	$1,400
	Mobilization/demobilizaton	$150,000	$16,000	No[5]	0.5	$75,000	$8,000
	Sheet piling - rental and installation	–	$203,000	No	1	–	$203,000
	Excavation of soil and backfill	$43,000	$50,000	Yes	0.14	$6,020	$7,000
	Ex situ treatment equipment and installation	–	$50,000	No	1	–	$50,000
	Start up costs	$5,000	$5,000	No	1	$5,000	$5,000
	Materials (amendments, shipping, utilities)	$297,000	$199,000	Yes	0.14	$41,580	$27,860
	Implementation labor	$300,000	$150,000	Yes	0.14	$42,000	$21,000
	Waste management and disposal	$25,000	$2,066,000	Yes	0.14	$3,500	$289,240
	Field and home office support	$90,000	$50,000	Yes	0.14	$12,600	$7,000
	Contractor oversight	$45,000	$57,000	Yes	0.14	$6,300	$7,980
	Reports	$50,000	$20,000	No	1	$50,000	$20,000
	Implementation Cost, $ Total	**$1,025,000**	**$2,876,000**			**$244,800**	**$647,480**
	Implementation Cost, $/yd^3	**$114**	**$320**			**$188**	**$498**

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1. After Harness and Konzuk (2014)
2. In the large site scenario, the treated soil volume is 9,000 cubic yards, based on the Harkness and Konzuk template site
3. In the small site scenario, the treated volume is 1,300 cubic yards, the approximate size of the treated soil zone at Site 17
4. The scale factor is set to 1.0 for fixed costs (i.e., not scalable) and set to 0.14 based on the size difference between small and large sites (0.14 = 1,300 yd^3 / 9,000 yd^3) for quantities that are assumed to change in proportion to the size of the site
5. The mobilization may be reduced for smaller-scale sites, where smaller scale (i.e., trackhoe-mounted) equipment may be used; a scale factor of 0.5 was assumed

The cost model (Table 12) includes estimates for the hypothetical site developed by Harkness and Konzuk (i.e., "large site") and scaled-down estimates for a Site 17 scenario (i.e., "small site"). In terms of treatment volume, the hypothetical site is 9,000 yd^3, which is about seven times larger than the treated source zone at Site 17 (1,300 yd^3). The costs shown in the "large site" model are directly from the Harkness and Konzuk model. Some of the key assumptions employed in the Harkness and Konzuk model are as follows.

- Mixing is implemented using a large-scale crane-mounted mixing system (as described by Olson et al. 2012) equipped with a 10-ft diameter mixing auger.
- Soil mixing would be completed over a period of 25 to 30 days, with 8 to 10 workers on site during mixing.

- The soil mixing material cost assumes treatment with 2% ZVI and bentonite for 195 metric tons (213 tons) of ZVI and bentonite, with unit costs of $860 and $275 per metric ton, respectively.

For a detailed discussion of additional assumptions employed in this cost model, the reader is referred to Harkness and Konzuk (2014).

For the small-site scenario, the cost model indicates which cost elements were assumed to be scalable, and the scale factor employed. Non-scalable cost elements do not change with the size of the site, thus a scaling factor of 1.0 was used. Scalable factors are assumed to change in proportion with the size of the site; in this case, the scaling factor is calculated as 1,300 yd^3 / 9,000 yd^3 = 0.14. An exception to these scaling factors is mobilization, for which smaller-scale equipment is available for smaller sites. A scaling factor of 0.5 was assumed to apply to the Site 17 ("small site") scenario.

7.1.2 ZVI-Clay Cost Drivers

From the cost model, the primary factor driving remediation cost is the size of the site. Other important factors that may affect implementation costs include the quantity of contamination present on the site (i.e., material costs) and time required for mixing (i.e., implementation labor). In highly contaminated sites, a higher concentration of ZVI may be required. In a summary of field applications (Olson 2014), typical target concentrations of ZVI range from 1 to 3%, regardless of initial contaminant concentration. From the cost model shown in Table 12, a variation in material costs by ±50% will affect the overall project cost much less than site size. Similarly, implementation of ZVI-Clay Soil Mixing may be complicated by site-specific circumstances such as obstructions to mixing (surface or buried) or challenging geology (e.g., overconsolidated clays). Such complications may increase the time required for mixing, thus increasing the implementation labor cost by (estimated) 50 to 100%.

7.1.3 ZVI-Clay Cost Analysis

The cost model shows a comparison between ZVI-Clay Soil Mixing and excavation, and also compares large- and small-site scenarios. Costs are shown on a "$ Total" and "$/$yd^3$" basis. In the large-site scenario, the costs of ZVI-Clay Soil Mixing and excavation are $114 and $320 per yd^3, respectively. In the small-site scenario, the costs of ZVI-Clay Soil Mixing and excavation are $188 and $498 per yd^3, respectively. In both large- and small-site scenarios, the estimated cost of ZVI-Clay Soil Mixing is less than half that of excavation. On a unit-volume basis, application of ZVI-Clay Soil mixing appears much cheaper for larger sites. This is due, in part, to the cost of equipment mobilization, which does not scale down in proportion to the site size.

Harkness and Konzuk also calculated 30-yr net present value (NPV) costs for each of the technologies evaluated, including costs for design elements shown above (design and capital) plus injection and long-term monitoring over 30 years. The result of this comparison is summarized in Table 13. The analysis suggests that ZVI-Clay Soil Mixing is less expensive than most related technologies. The cost is comparable (slightly higher) than that estimated for EISB. The ZVI-Clay Soil Mixing technology is completed in a single pass, and is assumed to be completely implemented in less than one year (in the case of Site 17, implementation was completed in two weeks); whereas EISB requires multiple injections and will require several years to implement.

Table 13. Template Site Source-Zone Remediation Cost Estimates[1]

Source-Zone Remediation Technology	NPV Cost
ZVI-Clay Soil Mixing	$1,514,000
EISB	$1,449,000
ISCO	$2,670,000
Thermal Remediation	$2,585,000
Excavation	$3,004,000

1 - Summary of results presented by Harkness and Konzuk (2014), comprising 30-year NPV cost of implementing the remedy. Cost elements included for all of the treatments include design, implementation (capital), and 30-year monitoring for all treatments. Five annual injection events were assumed for ISCO, using sodium permanganate as an oxidant, and two injection events over three years were assumed for EISB.

7.2 C_3 TECHNOLOGY COST ASSESSMENT

A potential limitation to wider-scale commercial application of C_3 for site characterization involves the cost for implementation and sample analysis. Until recently, the time required for freezing of cores *in situ* was prohibitive. However, through development conducted under SERDP-funded project ER-1740 (and similar projects conducted concurrently by the ER-1740 PIs), the time required to freeze each core was reduced from approximately 45 to 6 minutes (Sale et al. 2016). This time reduction removed a primary barrier towards commercialization. Although cryogenic coring remains more expensive than traditional coring, due to specialized equipment and need for LN, the cost difference has been largely minimized to necessary equipment and materials. Another cost element for C_3 characterization involves high-resolution multi-parameter sample analysis. The cost of analysis is generally similar for high-resolution analysis, whether using traditional or cryogenic core collection. However, C_3 offers the potential for preservation of certain parameters (e.g., biological community and gaseous analytes), such that an opportunity for additional analysis exists.

The C_3 technology, which was used for the high-resolution performance assessment described herein, has not been subject to a published detailed cost evaluation. To that end, costs involved in C_3 implementation and sample processing were tracked throughout this project. The following cost evaluation was developed with the objective of comparing C_3 to conventional coring, and evaluating based on the desired frequency of depth-resolved samples.

7.2.1 C_3 Cost Model

The cost model is presented in Table 14. The model includes two primary cost elements: core collection and core processing. The core-collection cost model is shown for both cryogenic and traditional core collection. Two scenarios for core processing are shown, one for in-house analysis and the other for commercial analysis. In-house analysis is based on the processing and analytical procedures conducted at the CSU laboratory, as was completed for this project. The commercial analysis assumes that preliminary processing will be conducted in-house, and the core subsamples will then be sent to a commercial laboratory for analysis. Specific details for each of these cost elements are discussed below. Additional costs that may be incurred, such as design, planning, permitting, and field oversight, are site specific and are not included in this evaluation.

Table 14. C_3 Cost Model

Cost Element	Item Description	Cryogenic coring				Traditional coring		
		Unit	Quantity	Unit Cost	Total Cost	Quantity	Unit Cost	Total Cost
Core Collection	Mobilization and Demob	LS	1	$2,400	$2,400	1	$2,400	$2,400
	Safety Meetings/Standby	Hr	8.5	$150	$1,275	8.5	$150	$1,275
	Crew Travel - Daily	Hr	4.5	$125	$563	4.5	$125	$563
	Hollow Stem Auger Drilling	Ft	34.5	$25	$845	132	$25	$3,234
	Cryogenic Coring (2.5-ft sections)	Ea	39	$550	$21,450	0	$285	$0
	Abandon Borings w/ Bentonite Chips	Ft	120	$12	$1,440	120	$8	$960
	Decontamination	Hr	4.5	$160	$720	4.5	$160	$720
	Support Vehicle Rental	Day	13	$125	$1,625	13	$125	$1,625
	Per Diem	Day	13	$500	$6,500	13	$500	$6,500
	Steam Cleaner/Decon Pad	LS	1	$500	$500	1	$500	$500
	Total				**$37,318**			**$17,777**
Core processing with in-house analysis	Laboratory sample preparation	Ea	150	$31.25	$4,688	150	$31.25	$4,688
	Processing	Ea	150	$31.25	$4,688	150	$31.25	$4,688
	Analysis - labor	Ea	150	$120	$18,000	150	$120	$18,000
	Analysis - instrument	Ea	150	$25	$3,750	150	$25	$3,750
	Total				**$31,125**			**$31,125**
Core processing with commercial analysis	Processing	Ea	150	$125	$18,750	150	$125	$18,750
	Analysis - VOCs (EPA 8260)	Ea	150	$70	$10,500	150	$70	$10,500
	Analysis - methane, ethane, ethylene	Ea	150	$85	$12,750	150	$85	$12,750
	Analysis - inorganic parameters	Ea	150	$65	$9,750	150	$65	$9,750
	Analysis - ferrous and total iron	Ea	150	$22	$3,300	150	$22	$3,300
	Total				**$55,050**			**$55,050**
Total - with In-House Analyis					**$68,443**			**$48,902**
Total - with Commercial Analyis					**$92,368**			**$72,827**

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Cost Element: Core Collection. Items included under this cost estimate are based on the costs tracked during the Site 17 field effort. Thus, the quantities presented in the cost model are based on a similar level of data collection to that conducted at Site 17 (i.e., cores collected from six locations, with a total sampled interval of approximately 100 ft). Mobilization and demobilization includes costs incurred for transporting the drilling crew and equipment from Fort Collins, Colorado to Site 17, Maryland. For the cost model, assumed components of mobilization include mileage ($5.50/mile), per diem ($500/day), and support vehicle rental ($150/day); the site model is based on a site that is 100 miles away (200 miles round trip), requiring one day each for mobilization/demobilization. Line items for (a) safety meetings/ standby, (b) daily crew travel, and (c) decontamination include hourly cost for the associated activities. Hollow-stem auger drilling includes cost of using the hollow-stem auger rig (which was described in Section 5.4.1), where cryogenic coring was not conducted. The line item for Cryogenic Coring covers all costs associated with collecting each 2.5-ft section of frozen core.

This line item includes C_3-specialized equipment, LN, and an extra person on site for drilling. The C_3-specialized equipment includes use of the modified continuous sampler (Figure 16) and LN circulation system. Boring abandonment includes filling borings with bentonite chips. A support vehicle consisted of a moving van (Figure 15) that was on site throughout drilling activities. The support vehicle was used to shuttle LN cylinders between the staging area and drilling location. A steam cleaner/decon pad included equipment used to generate steam for decontamination of equipment before demobilization.

Cost Element: Core Processing with In-House Analysis. This cost element includes labor and analytical costs for processing of frozen cores and completing the primary sample analyses at the CSU laboratory. Laboratory sample preparation includes time for preparing sample jars and equipment for frozen core processing. For preparation time, a total of 132 hours were recorded, including a combination of undergraduate ($15/hr, burdened with fringe) and research associate ($80/hr, burdened) time. On the basis of 132 hours of prep time for 150 samples, an estimated time of 1.0 hr of labor per sample, at a combined rate of $31.25/hr (25% research associate and 75% undergraduate), was assumed. Processing includes time required to cut cores and perform extractions at the time of processing (e.g., the methanol and aqueous extractions, as described in Section 5.6). Based on the recorded time required (140 hr) for CSU to generate approximately 150 samples, a processing time of 1.0 hr per sample was assumed, at a combined rate of $31.25. Labor for analysis includes time to complete analyses. An analysis labor time of 1.5 hr per sample was assumed, at a research associate rate of $80/hr. Analysis labor includes time for preparation and analysis of instrument calibration standards. Instrument analysis includes cost for instrument time, at a cost of $17 per sample; this includes $7 per sample for GC/MS analysis, $5 per sample for IC analysis, and $7 per sample for GC/FID analysis.

Cost Element: Core Processing with Commercial Analysis. This cost element includes labor and analytical costs for processing of frozen cores and sending samples to an external laboratory for analysis. This analysis assumes 1 hr of prep time per sample, including cutting frozen core and packaging subsamples for analysis by an external laboratory. It was assumed that processing would be completed by experienced field personnel at a rate of $125/hr. A similar processing time is assumed for cryogenic and conventional coring, as subsamples will need to be individually prepared and packaged for analysis. Analysis rates for VOCs (via EPA method 8260), gaseous products, inorganic parameters, and iron (ferrous and total) are shown in Table 14.

7.2.2 C_3 Cost Drivers

Following the cost model, a key cost driver for C_3 implementation is the sample analysis. The cost of sample analysis is determined by the number of locations analyzed and desired sample resolution. Site-specific circumstances and characterization budget may be the key factors considered in deciding the number of locations and sampling resolution. For example, at Site 17, the number of locations was determined by the project objectives, which included assessment of biogeochemical conditions in source-zone soils (performance objective 2) and generating data that improves understanding of downgradient processes (performance objective 3). From this, two locations were selected from within the treated soil zone, representing low- and high-concentration zones. Four locations were selected downgradient to provide transect data aligning with two existing monitoring wells. The sampled interval was selected based on existing site concentration data and geologic logs.

The target sampling resolution utilized at Site 17 was 6-in. per sample; this resolution is considered high, but was implemented for this project to support the performance objectives, particularly supplementation of existing performance remediation data with high-resolution data (performance objective 1) and to ensure that low-*k* zones were adequately characterized to support long-term remedy decisions.

From this, when considering implementation of C_3 characterization at future sites, optimal use of the C_3 characterization will involve evaluation of known data. Thus, cryogenic coring may generate comprehensive, high-resolution data that supplements existing data and addresses potential data gaps, such as processes occurring within low-*k* zones. The following cost analysis includes a comparison of cryogenic versus conventional coring, with analysis conducted at varying spatial resolution.

7.2.3 C_3 Cost Analysis

A cost analysis was conducted to compare cryogenic coring to conventional coring at varying depth-discrete sampling resolutions. The evaluation also compares in-house analysis (as conducted by CSU for the Site 17 project) with up-scaled cost using a commercial laboratory for analysis. This analysis includes basic geochemical analyses; specialized analyses (e.g., biological characterization and reactivity testing) that may be implemented as needed for site-specific data needs are not included. For example, the reactivity testing conducting herein (Section 5.6.6) was customized for a ZVI-mixed soil zone. The cost evaluation, shown in Table 15, is directly based on the cost model, developed in Section 7.2.1.

The cost model implies that the cost of sample collection and analysis are independent, i.e., the cost of cryogenic coring at six locations are independent of the resolution at which the cores are sub-sampled. Following this cost model, the implementation cost of C_3 is approximately 70% higher than the cost of conventional coring. The difference includes materials (e.g., LN) and use of specialized equipment (e.g., modified sample barrel). For the high-resolution sample analysis, the commercial analytical costs are approximately 80% higher than in-house analytical costs. A substantial amount of flexibility is inherent in the analytical costs, as the specific analyses and spatial resolution can be determined based on a balance between project budget and site-specific data needs. For future C_3 applications, the commercial cost difference could possibly be reduced through development of streamlined/customized analyses, in cooperation with a commercial laboratory.

The cost differential for cryogenic coring, coupled with high-resolution analysis, may be justified when considering the potential for long-term remediation cost savings. For example, contaminant mass within low-*k* zones may have a substantial effect on injection-based remedies. Referring to the comparison presented by Harkness and Konzuk, the need for repeated injections was a substantial cost driver for EISB and ISCO. Detailed characterization of contaminant mass residing within the low-k zones would support this decision and inform the assumptions made in the cost evaluation. When considering remedies that may cost on the order of $1.5 to $3.0 million (Table 13), comprehensive data generated via C_3 may be of high importance. Data for gaseous degradation products, may also affect how large plumes are managed. With additional development, data generated via cryogenic coring may improve our ability to quantify degradation rates and thus improve longevity estimates for MNA and/or engineered remedies.

Table 15. C_3 Cost Analysis

Cost Element	Item Description	Cryogenic coring			Traditional Coring		
		0.5 samples/ft	1 sample/ft	2 samples/ft	0.5 samples/ft	1 sample/ft	2 samples/ft
Core Collection	Mobilization and Demob	$2,400	$2,400	$2,400	$2,400	$2,400	$2,400
	Safety Meetings / Standby	$1,275	$1,275	$1,275	$1,275	$1,275	$1,275
	Crew Travel - Daily	$563	$563	$563	$563	$563	$563
	Hollow Stem Auger Drilling	$845	$845	$845	$3,234	$3,234	$3,234
	Cryogenic Coring (2.5-ft sections)	$21,450	$21,450	$21,450	$0	$0	$0
	Abandon Borings	$1,440	$1,440	$1,440	$960	$960	$960
	Decontamination	$720	$720	$720	$720	$720	$720
	Support Vehicle Rental	$1,625	$1,625	$1,625	$1,625	$1,625	$1,625
	Per Diem	$6,500	$6,500	$6,500	$6,500	$6,500	$6,500
	Steam Cleaner/Decon Pad	$500	$500	$500	$500	$500	$500
	Total	**$37,318**	**$37,318**	**$37,318**	**$17,777**	**$17,777**	**$17,777**
Core processing with in-house analysis	Laboratory sample preparation*	$1,563	$3,125	$6,250	$1,563	$3,125	$6,250
	Processing*	$1,563	$3,125	$6,250	$1,563	$3,125	$6,250
	Analysis - labor*	$6,000	$12,000	$24,000	$6,000	$12,000	$24,000
	Analysis - instrument	$1,250	$2,500	$5,000	$1,250	$2,500	$5,000
	Total	**$10,375**	**$20,750**	**$41,500**	**$10,375**	**$20,750**	**$41,500**
Core processing with commercial analysis	Processing*	$6,250	$12,500	$25,000	$6,250	$12,500	$25,000
	Analysis - VOCs (EPA 8260)	$3,500	$7,000	$14,000	$3,500	$7,000	$14,000
	Analysis - methane, ethane, ethylene	$4,250	$8,500	$17,000	$4,250	$8,500	$17,000
	Analysis - inorganic parameters	$3,250	$6,500	$13,000	$3,250	$6,500	$13,000
	Analysis - ferrous and total iron	$1,100	$2,200	$4,400	$1,100	$2,200	$4,400
	Total	**$18,350**	**$36,700**	**$73,400**	**$18,350**	**$36,700**	**$73,400**
Total - with In-House Analyis		**$47,693**	**$58,068**	**$78,818**	**$28,152**	**$38,527**	**$59,277**
Total - with Commercial Analyis		**$55,668**	**$74,018**	**$110,718**	**$36,127**	**$54,477**	**$91,177**

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8.0 IMPLEMENTATION ISSUES

Implementation issues are discussed for both of the technologies used in this project.

Implementation of the ZVI-Clay Soil Mixing technology was described in detail in the Soil Mixing Completion Report (CH2M HILL 2013). The primary issues associated with implementation of the technology were related to actual or potential buried materials. Due to history of Site 17, potential for UXOs existed, thus UXO clearance over a relatively large area was required prior to soil mixing. In addition, buried wood was encountered over much of the area under Site 17, at a typical depth of 5 to 7 ft bgs. The buried wood, which was identified as "logs," was an obstruction that could not be mixed through. Thus, the wood was excavated prior to soil mixing, which also required removal of the surface soils. Aside from these issues, no other implementation issues were documented in the Soil Mixing Completion Report. In terms of effort required to achieve effective source-zone removal, implementation of soil mixing was a relatively rapid process, only requiring approximately two weeks of mixing time (excluding pre-mixing site preparation and post-mixing cleanup).

Issues were also encountered during the C_3 implementation. Primary issues included:

- Limited sample recovery in the mixed-soil zone (discussed in Section 6.4),
- Buried wood affected sample recovery (discussed in Section 5.4),
- Freezing of sampling equipment down hole (discussed in Section 6.4),
- Freezing of core liner in sample barrel (discussed in Section 6.4), and
- Running out of LN (discussed in Section 6.4).

Each of these issues, except the poor recovery within the mixed soil zone, was satisfactorily resolved. The limited mixed-zone recovery was likely related to softness of the bentonite-mixed soils, which limited soil entry into the core barrel. This issue was not attributed to the cryogenic coring process, i.e., the same issue would likely have occurred using standard soil-core collection procedures. For future implementation of cryogenic coring in soft soils, additional modifications to the sampling apparatus may be required to improve recovery.

Where encountered, the buried wood limited sample recovery but was overcome by using the auger to bore through the woody layer. The lack of surface samples in these locations did not create significant data gaps at Site 17, as the primary contamination depth occurred below 8 ft bgs. As with the limited recovery in the mixed-soil zone, recovery issues associated with buried woody debris were not attributed to the cryogenic coring process, i.e., the same issue would likely have occurred using standard soil-core collection procedures.

Other issues, which resulted in minor delays, included (a) coring equipment freezing downhole, (b) freezing or binding of the core sample in barrel, and (c) running out of LN in the vicinity of sampling. Downhole freezing of coring equipment occurred in only one sample depth during soil-core collection activities at Site 17, and may have occurred due to circulation of LN too long. Freezing of the core sample in the barrel was the cause of minor delays (typically <10 min); when this occurred, the sample was removed by circulating steam through the LN circulation system to remove ice buildup; no major changes in implementation are recommended to address this issue, as the solution did not results in lengthy delays.

On one occasion, the readily available LN supply was completely consumed, and the cryogenic coring activities had to stop while the support vehicle retrieved more LN from the staging area. This issue was addressed by bringing an extra LN dewar to each new location.

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APPENDIX A POINTS OF CONTACT

Point of Contact Name	Organization Name Address	Phone Email	Role in Project
Dr. Mitchell Olson	Trihydro Corporation 1537 Riverside Ave Fort Collins, CO 80524	P: (970) 492-6022 E: molson@trihydro.com	Co-Principal Investigator
Dr. Wilson Clayton	W.S. Clayton, Ltd. 28599 Buchanan Dr., Evergreen, CO 80439, as contractor to Trihydro Corp.	P: (303) 679-3143 E: wilson@wsclayton.com	Principal Investigator
Dr. Tom Sale	Colorado State University 1320 Campus Delivery Fort Collins, CO 80523	P: (970) 491-8413 E: tsale@engr.colostate.edu	Tech support and oversight of laboratory processing and analysis
Dr. Susan DeLong	Colorado State University 1320 Campus Delivery Fort Collins, CO 80523	P: (970) 491-6606 E: susan.de_long@colostate.edu	Microbiological analysis support
Maria Irianni-Renno	Colorado State University 1320 Campus Delivery Fort Collins, CO 80523	P: (970) 491-8647 E: mmiriann@eagle.fgcu.edu	Field and laboratory support
Dr. Rick Johnson	Oregon Health & Science University Gaines Hall, Room 233 3181 SW Sam Jackson Park Rd Portland, OR 97239	P: (503) 346-3432 E: rick.johnson.phd@gmail.com	Tech support
Rick Rogers	Drilling Engineers, Inc. 1309 Duff Dr Fort Collins, CO 80522	P: (970) 484-5183 E: rick@drillingengineers.com	Drilling contractor

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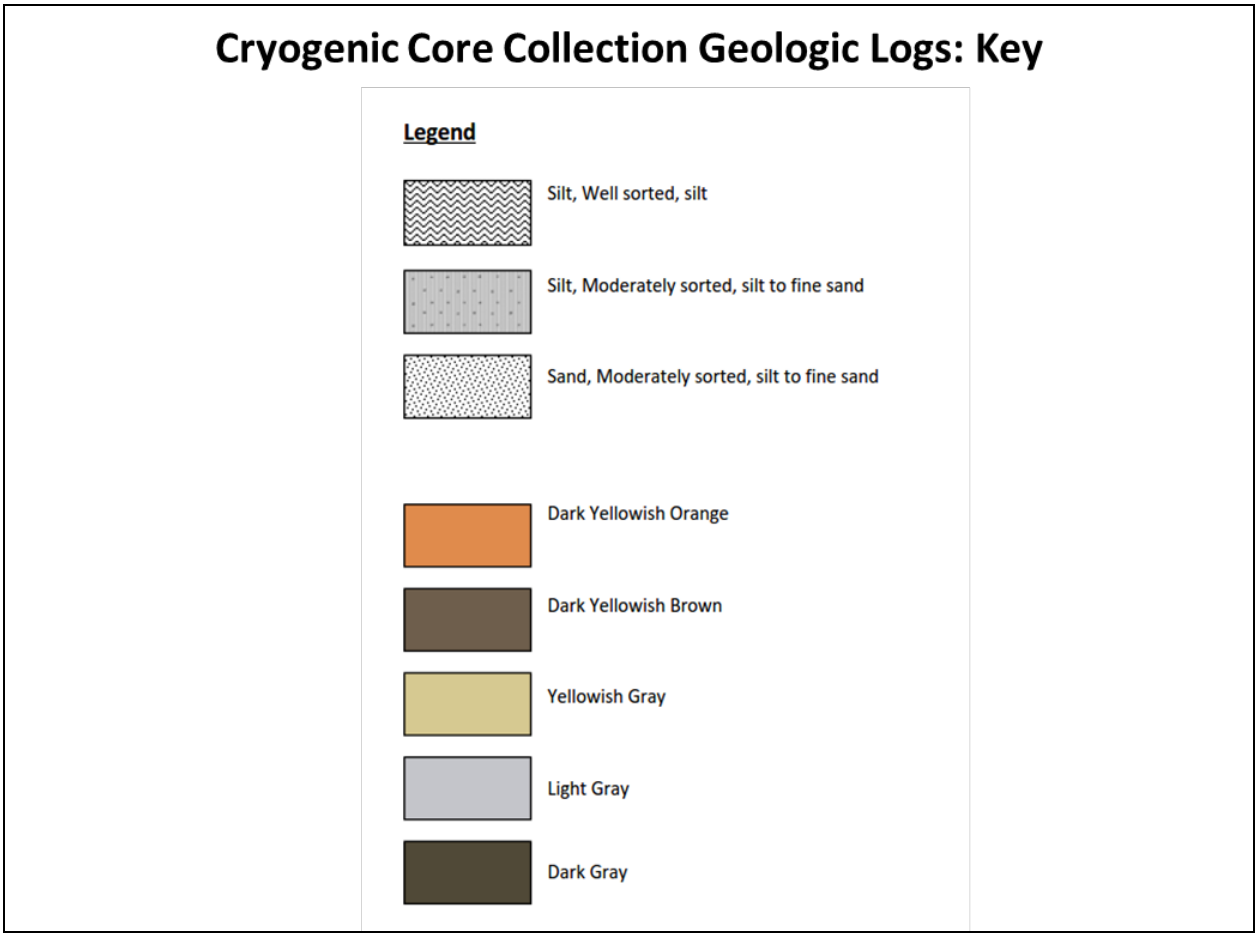
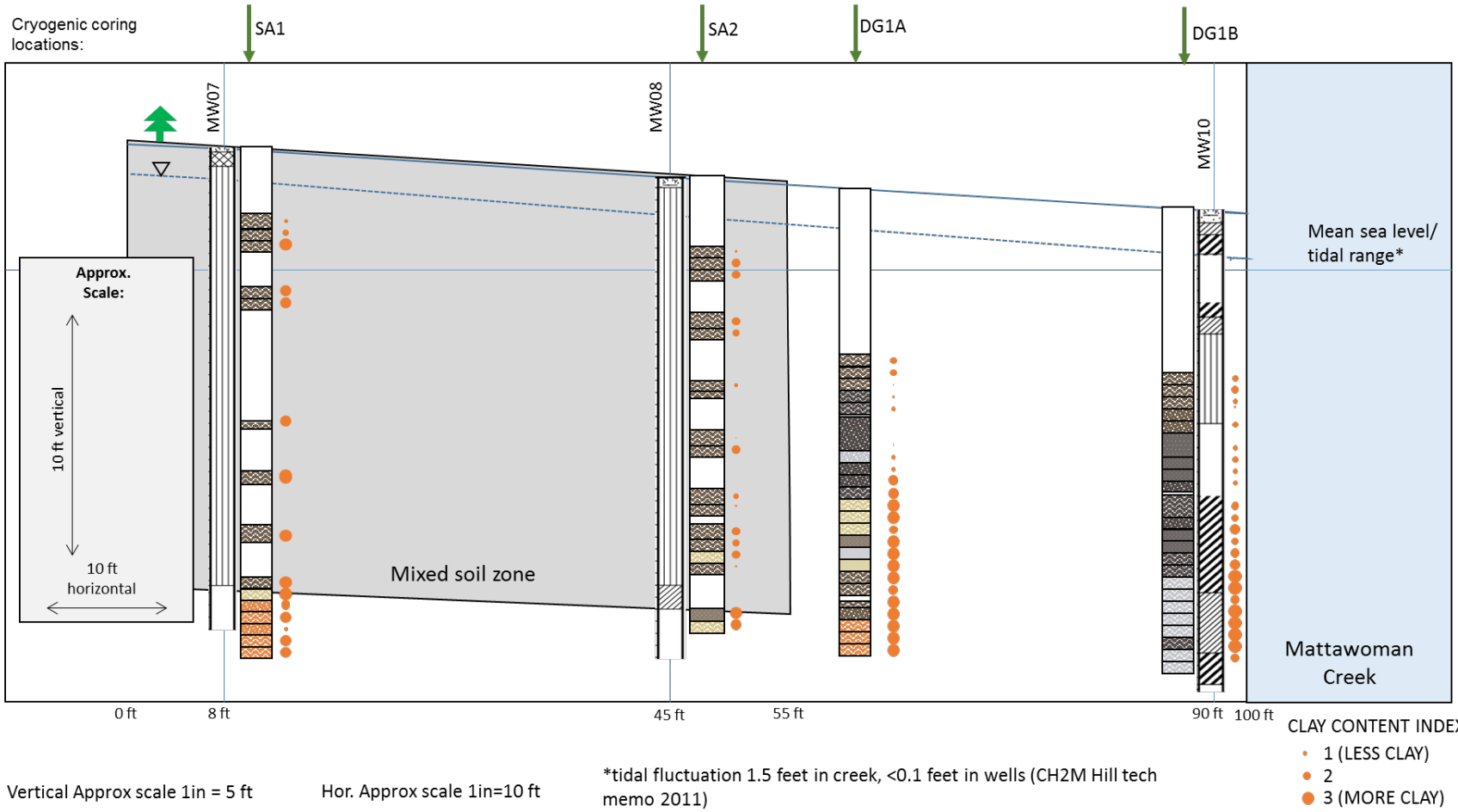
APPENDIX B GEOLOGIC LOGS

Geologic cross-section plots are shown in landscape orientation on the following pages.



Geology Data Cross Section: Transect DG1

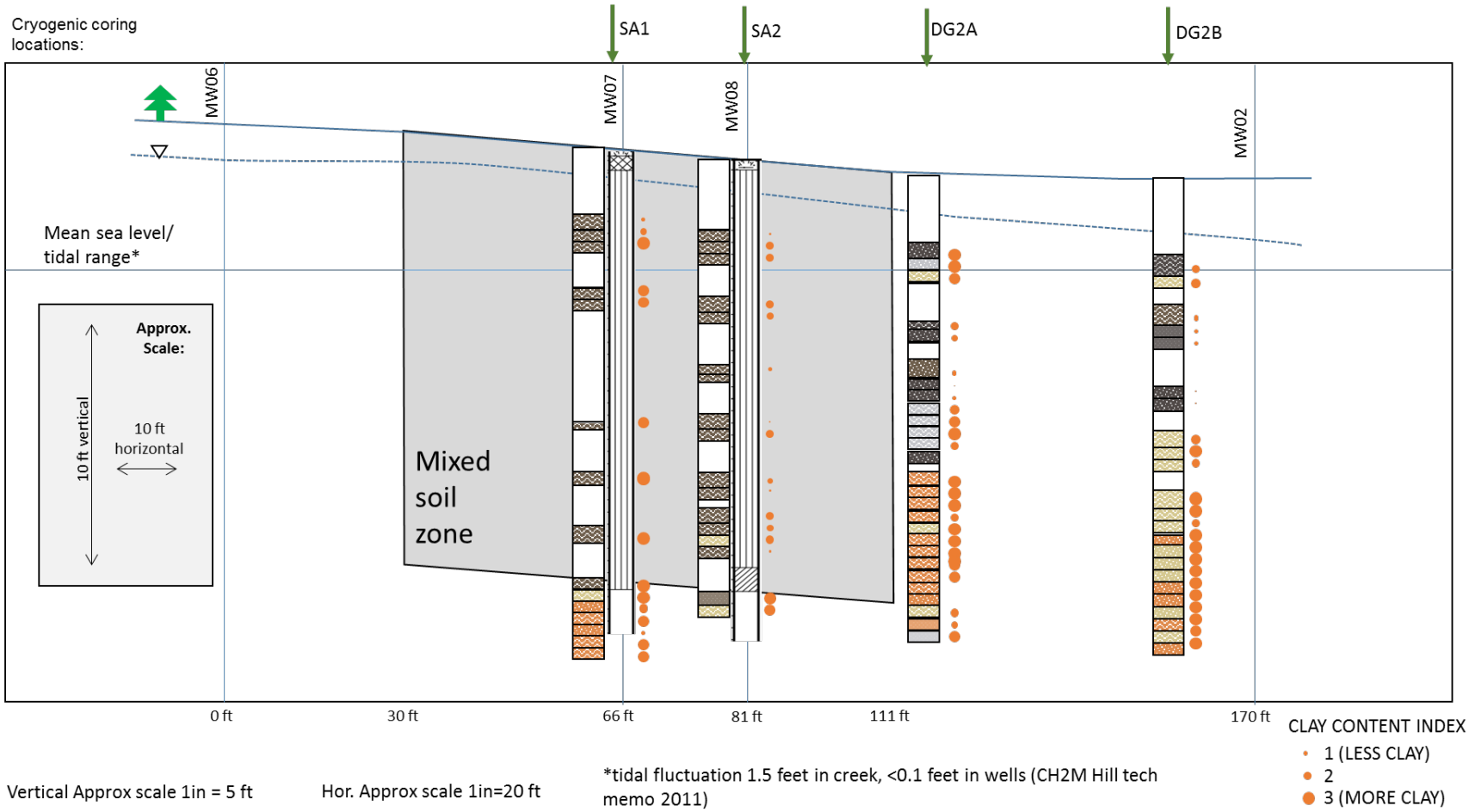


Vertical Approx scale 1in = 5 ft

Hor. Approx scale 1in=10 ft

*tidal fluctuation 1.5 feet in creek, <0.1 feet in wells (CH2M Hill tech memo 2011)

Geology Data Cross Section: Transect DG2



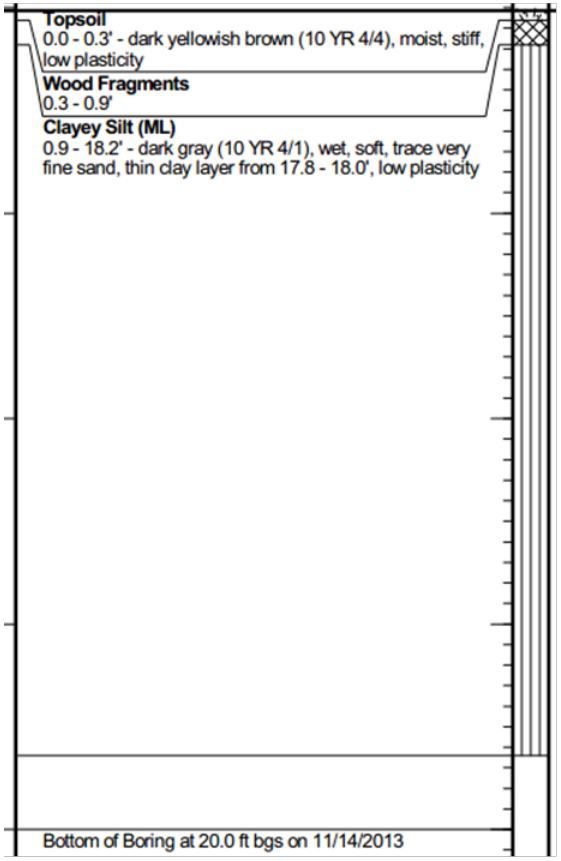
Vertical Approx scale 1in = 5 ft

Hor. Approx scale 1in=20 ft

*tidal fluctuation 1.5 feet in creek, <0.1 feet in wells (CH2M Hill tech memo 2011)

Existing Geologic Logs: Details

MW07*



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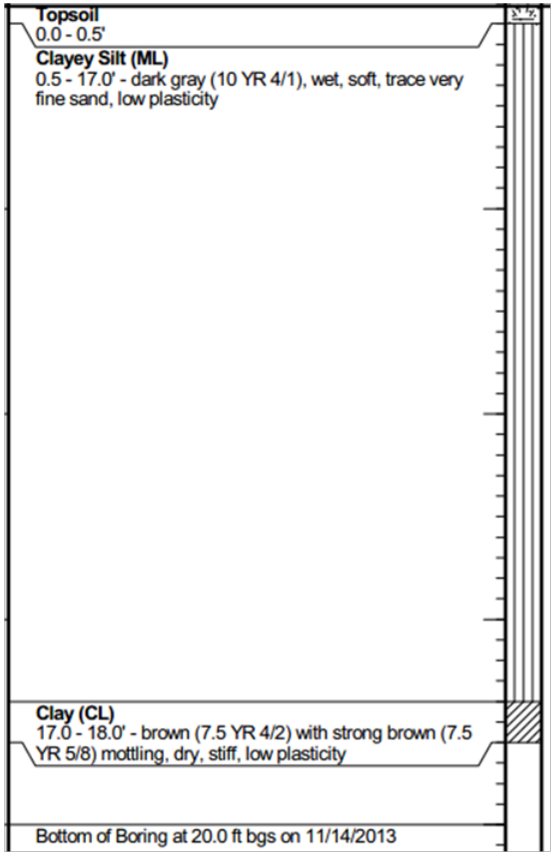

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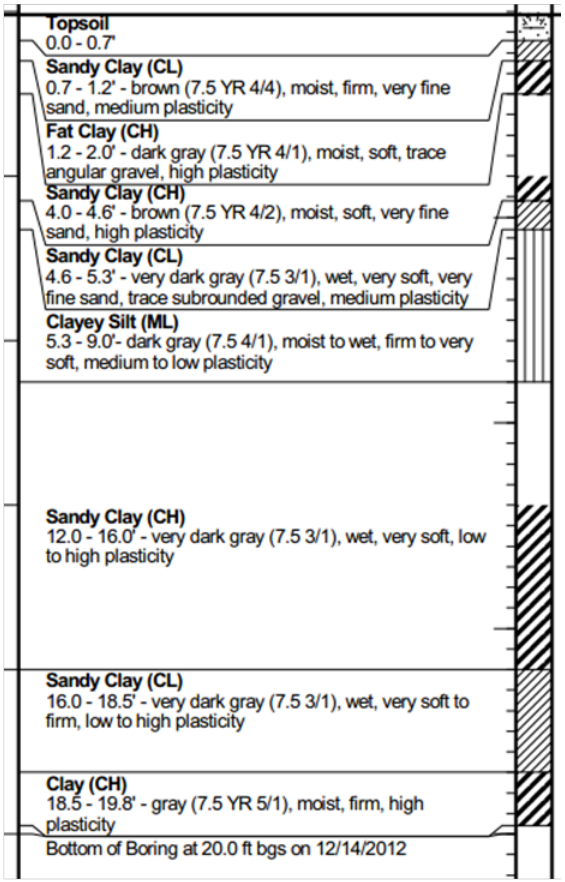
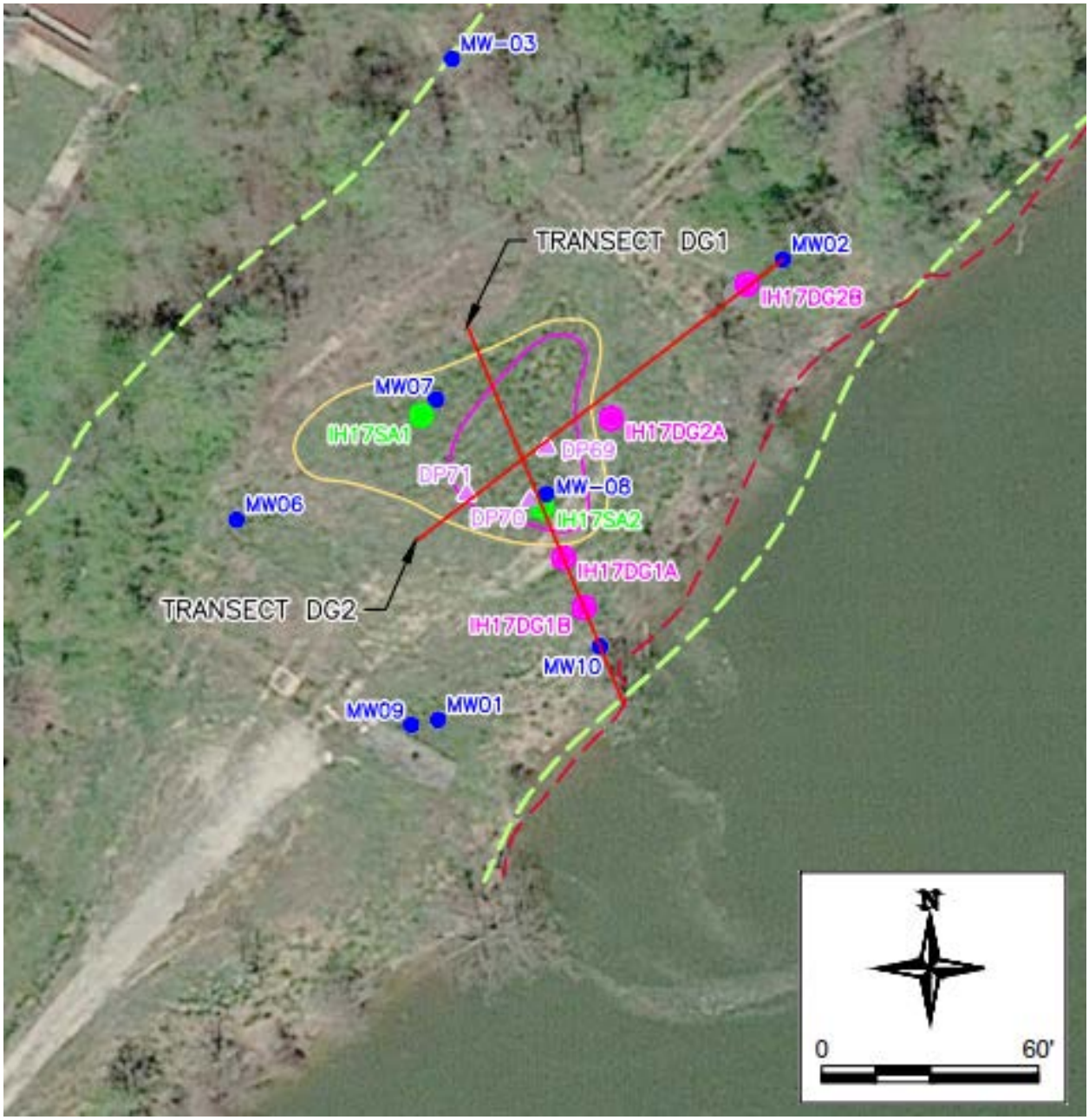
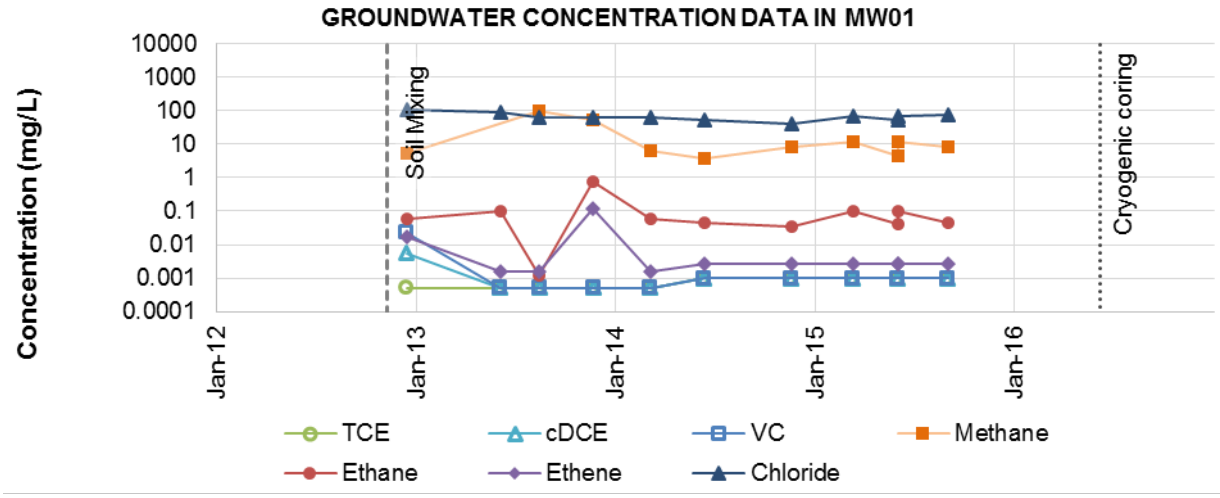


*CH2M HILL 2014

APPENDIX C PREVIOUSLY EXISTING GROUNDWATER DATA




GROUNDWATER CONCENTRATION DATA IN MW01
Concentration (mg/L)
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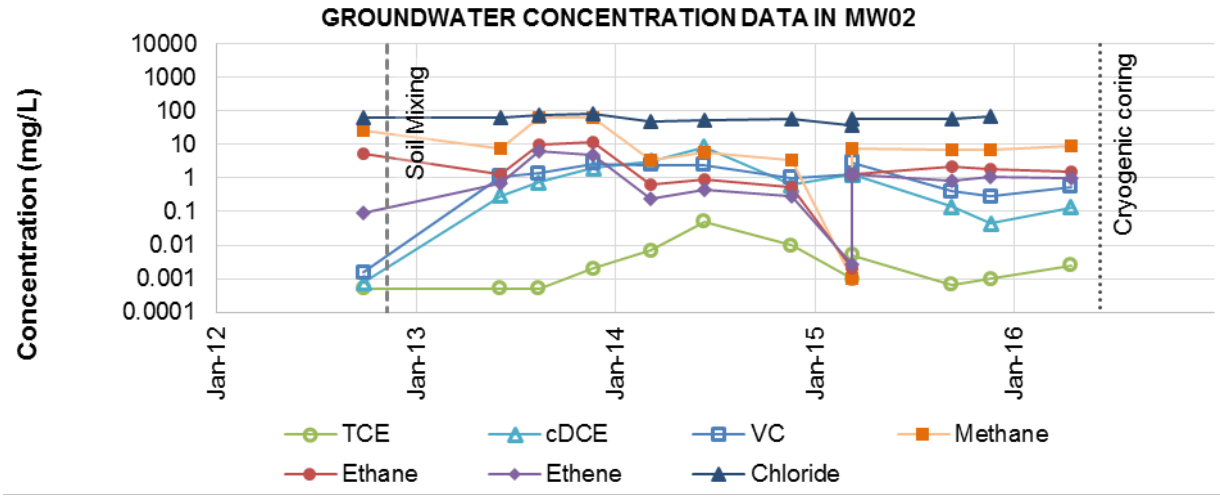
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride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Concentration (mg/L)
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1000
100
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1
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0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
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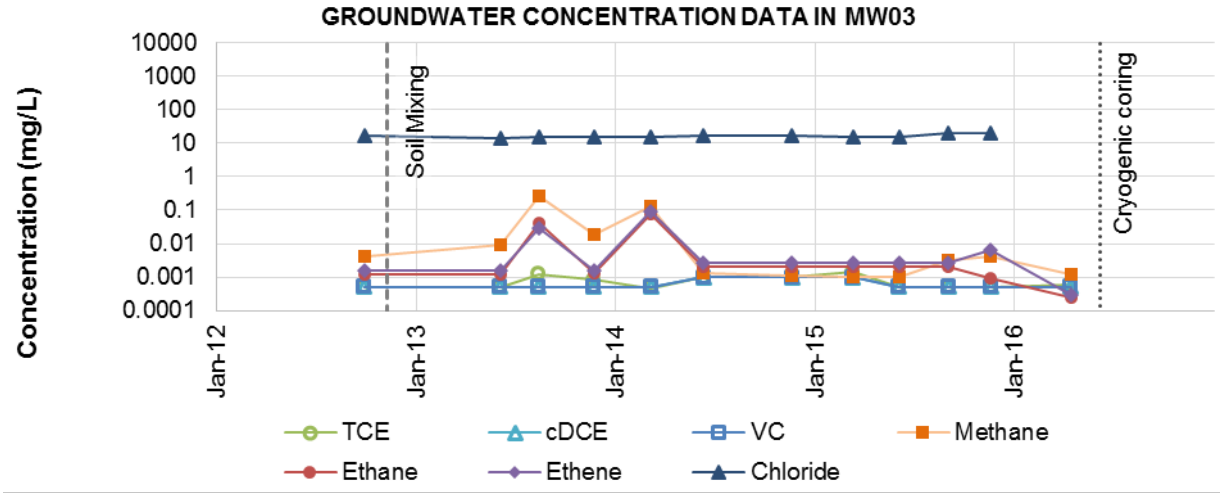
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride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Concentration (mg/L)
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0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
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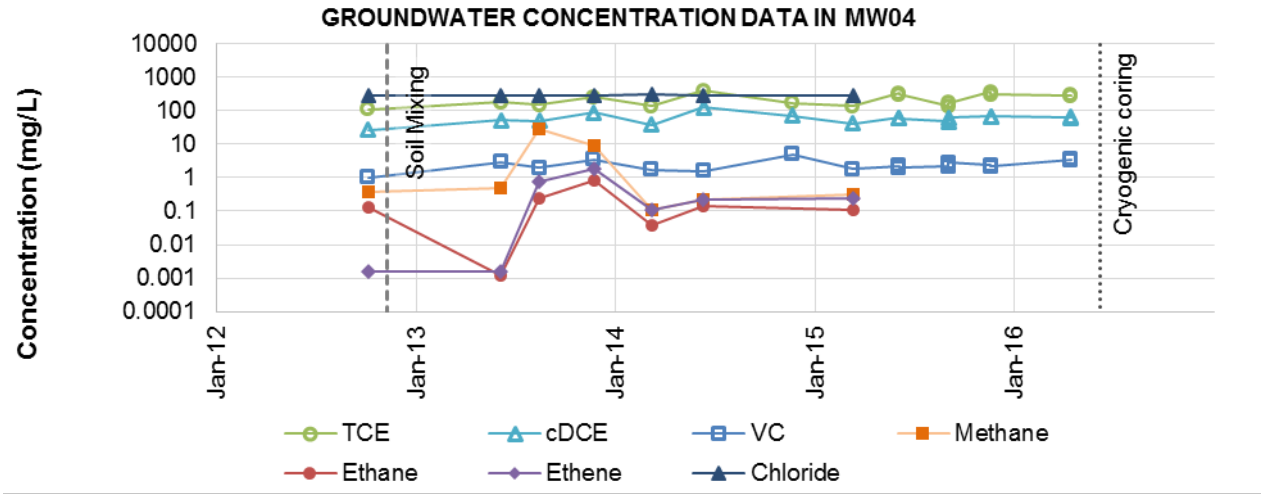
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW04
Concentration (mg/L)
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0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
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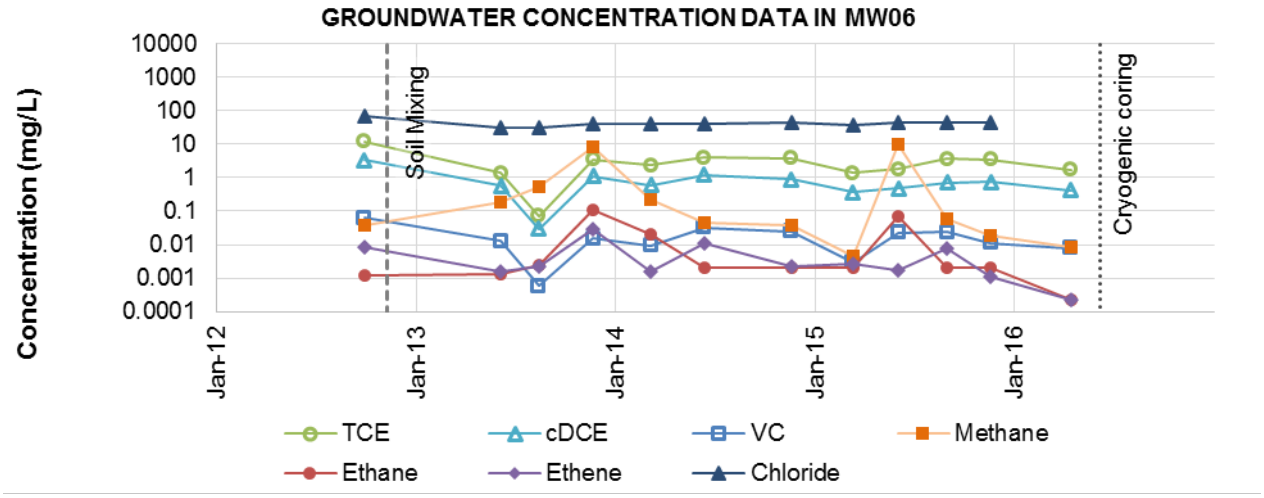
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW06
Concentration (mg/L)
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0.01
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0.0001
Soil Mixing
Cryogenic coring
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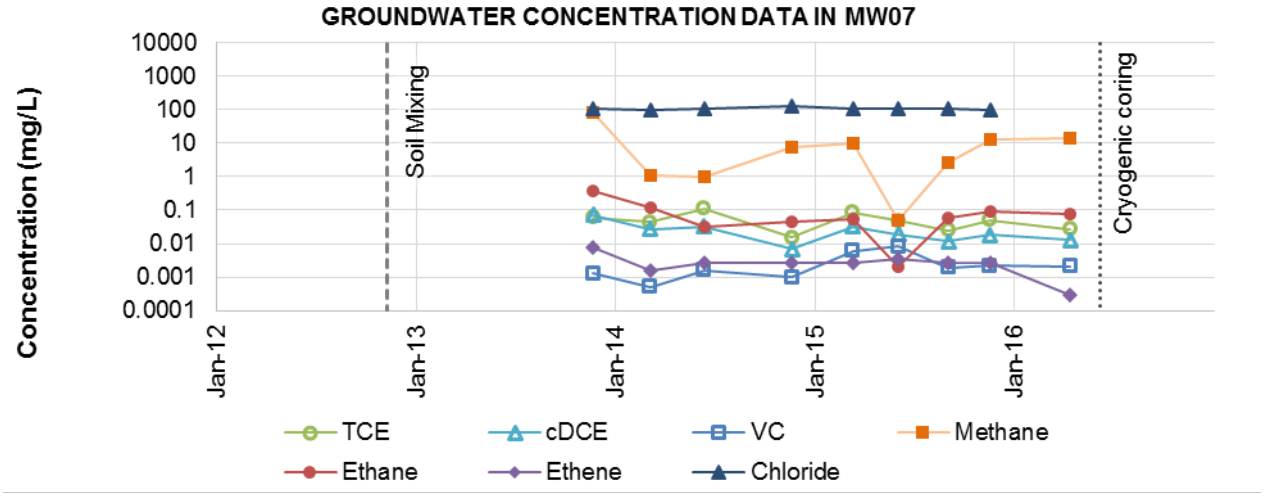
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW07
Concentration (mg/L)
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0.001
0.0001
Soil Mixing
Cryogenic coring
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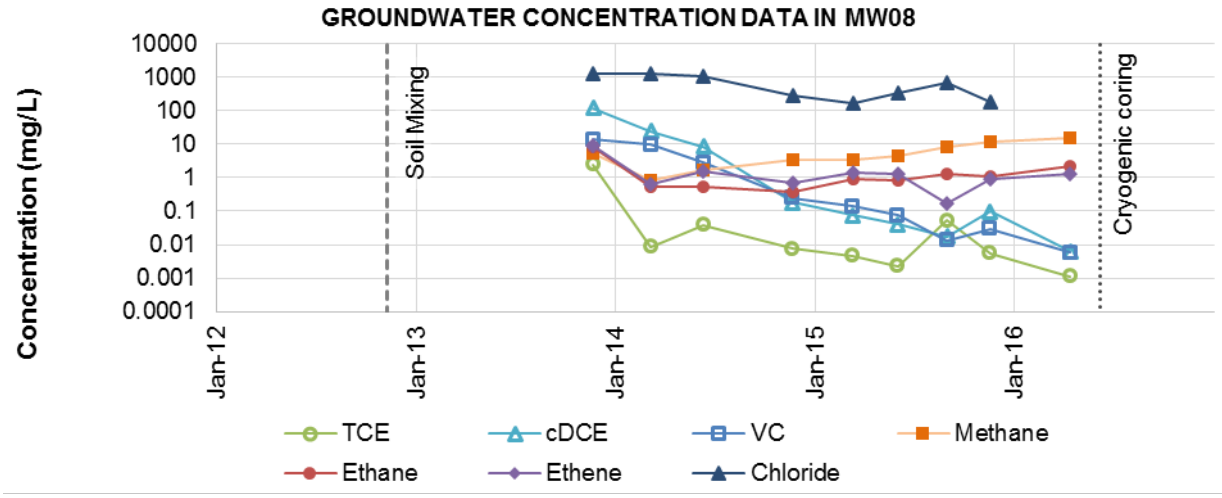
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW08
Concentration (mg/L)
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Soil Mixing
Cryogenic coring
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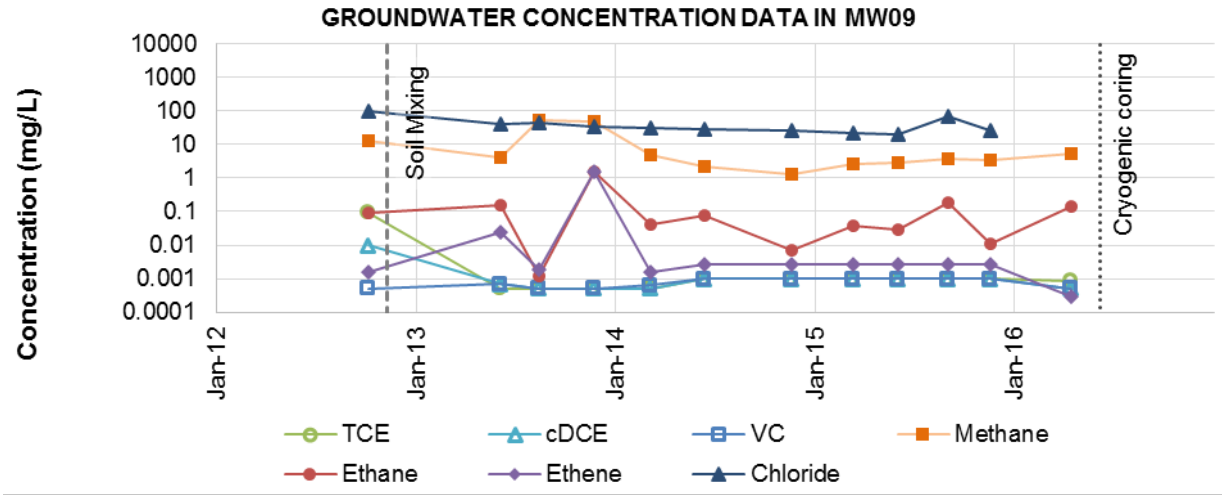
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW09
Concentration (mg/L)
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0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
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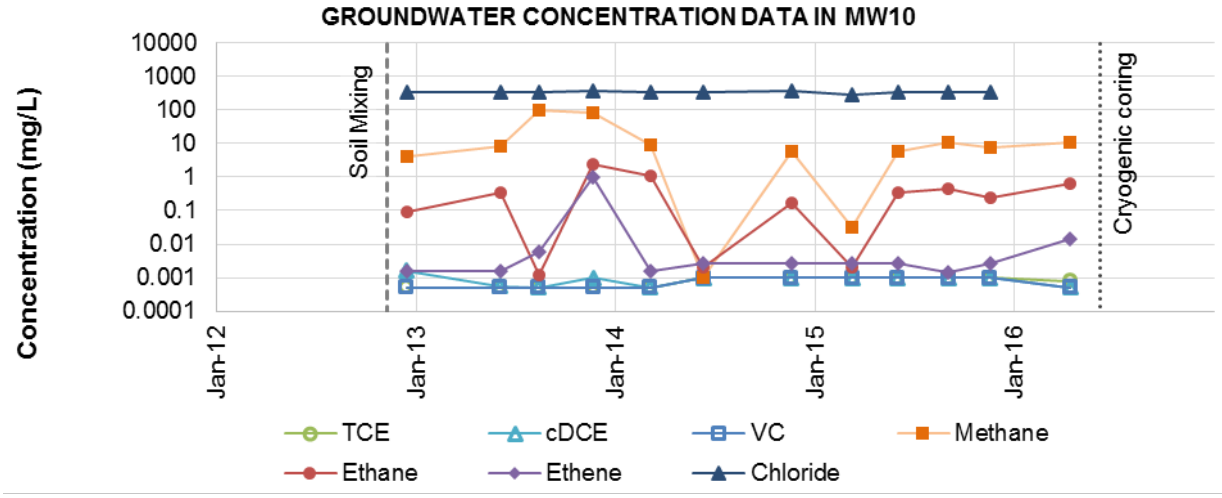
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW10
Concentration (mg/L)
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Soil Mixing
Cryogenic coring
Jan-12
Jan-13
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cDCE
VC
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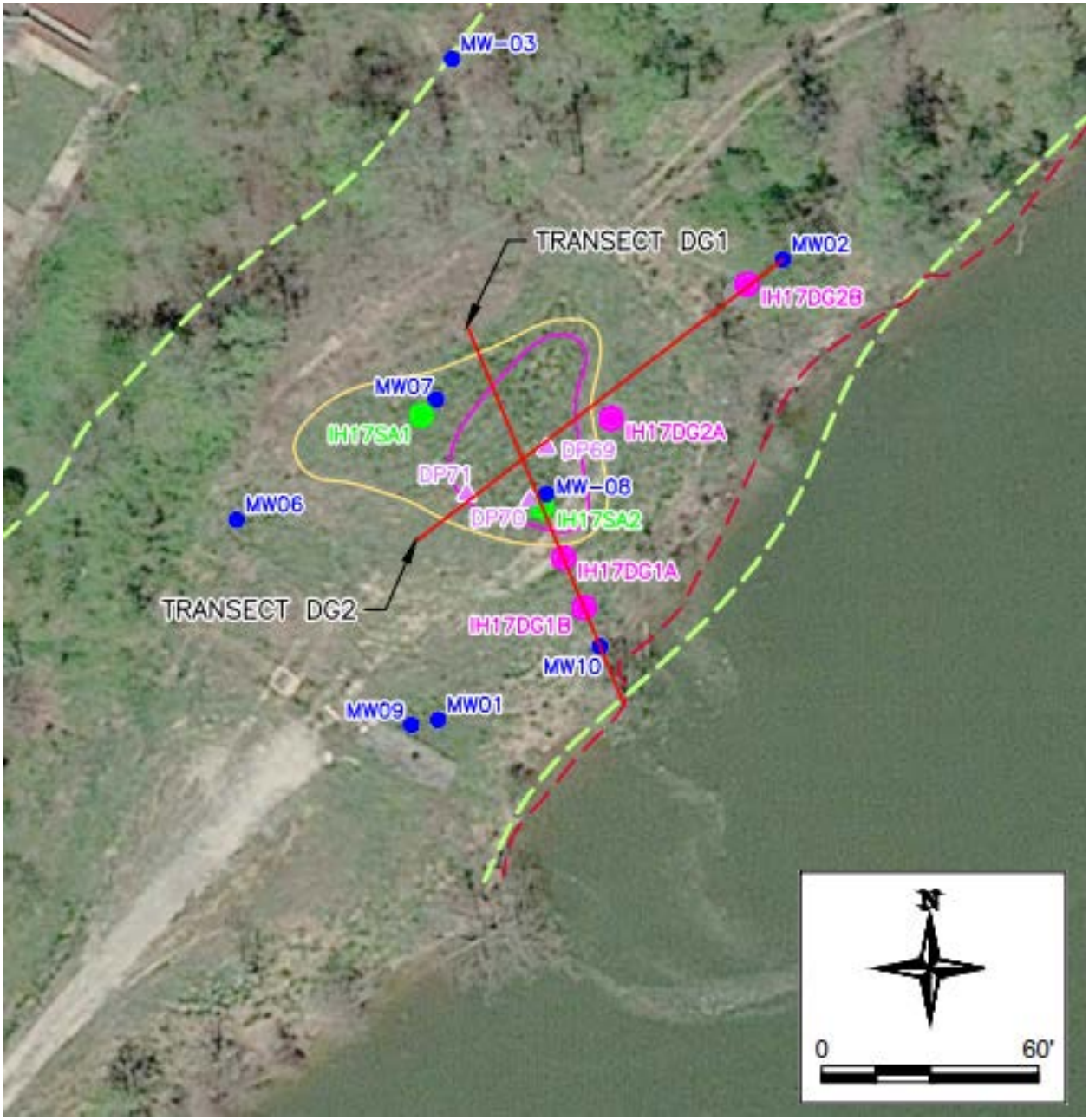
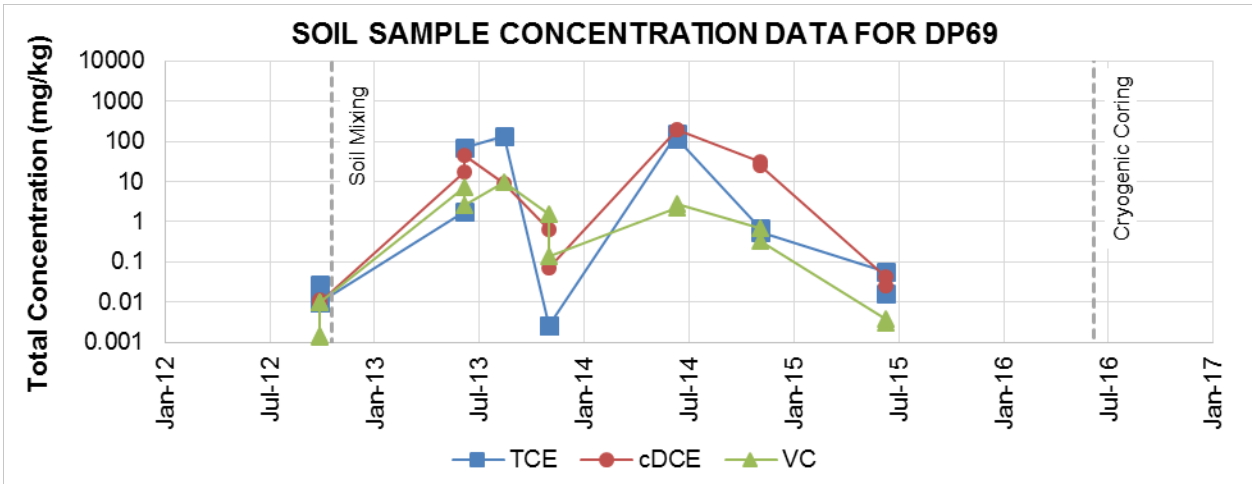
Ethane
Ethene
Chloride

APPENDIX D PREVIOUSLY EXISTING SOIL DATA

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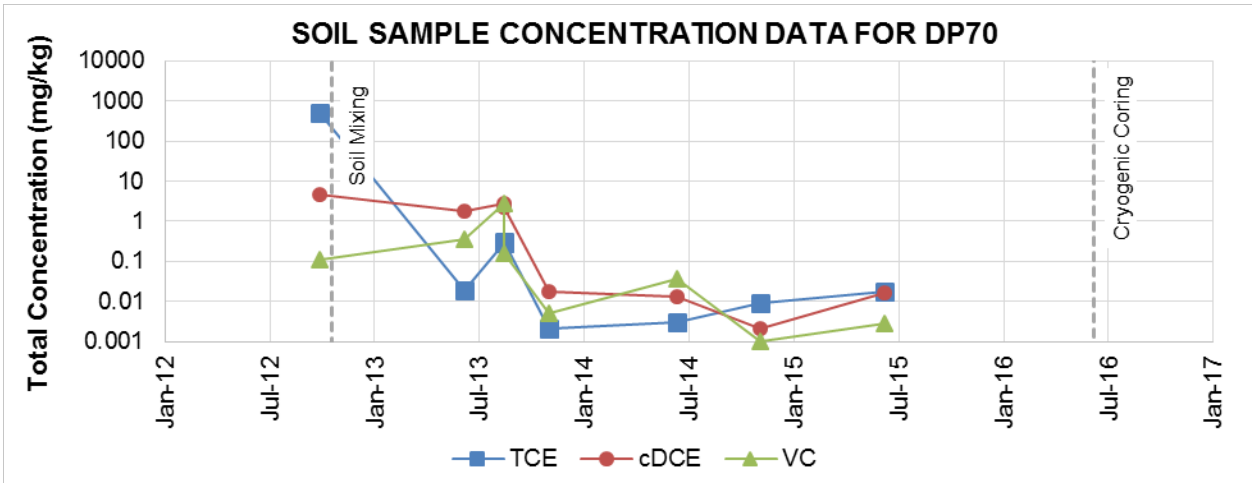
0.01
0.001
Soil Mixing
Cryogenic Coring
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
TCE
cDCE
VC


SOIL SAMPLE CONCENTRATION DATA FOR DP70
Total Concentration (mg/kg)
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0.01
0.001
Soil Mixing
Cryogenic Coring
Jan-12
Jul-12
Jan-13
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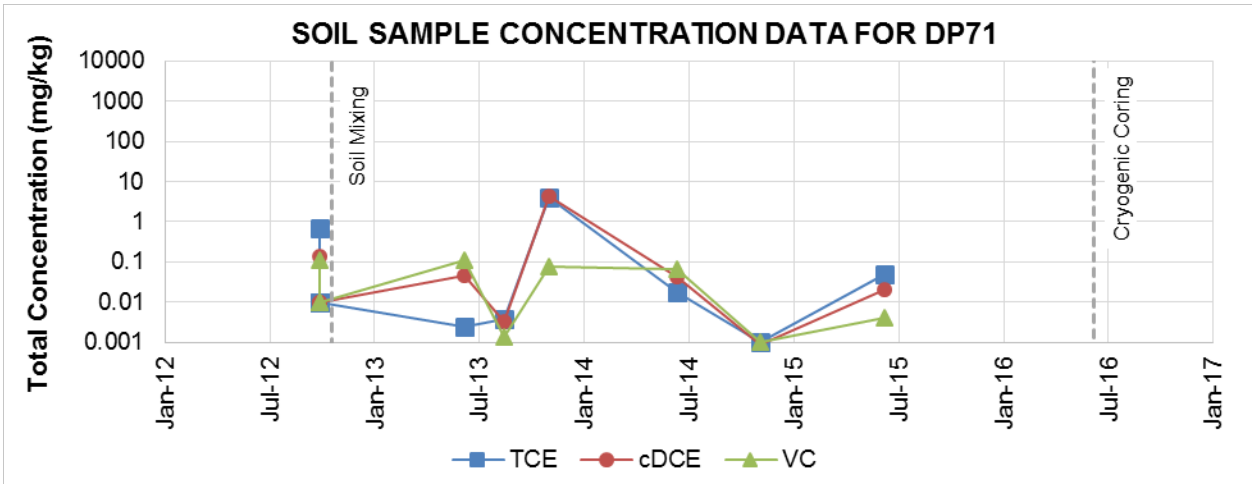
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
TCE
cDCE
VC


SOIL SAMPLE CONCENTRATION DATA FOR DP71
Total Concentration (mg/kg)
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0.1
0.01
0.001
Soil Mixing
Cryogenic Coring
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
TCE
cDCE
VC

APPENDIX E PHOTOGRAPHIC LOG


NITROGEN
NITROGEN
PENSKE


CENTRAL MINE
EQUIPMENT CO.


TRAL MINE
EQUIPMENT CO.


HONDA

APPENDIX F QUALITY ASSURANCE

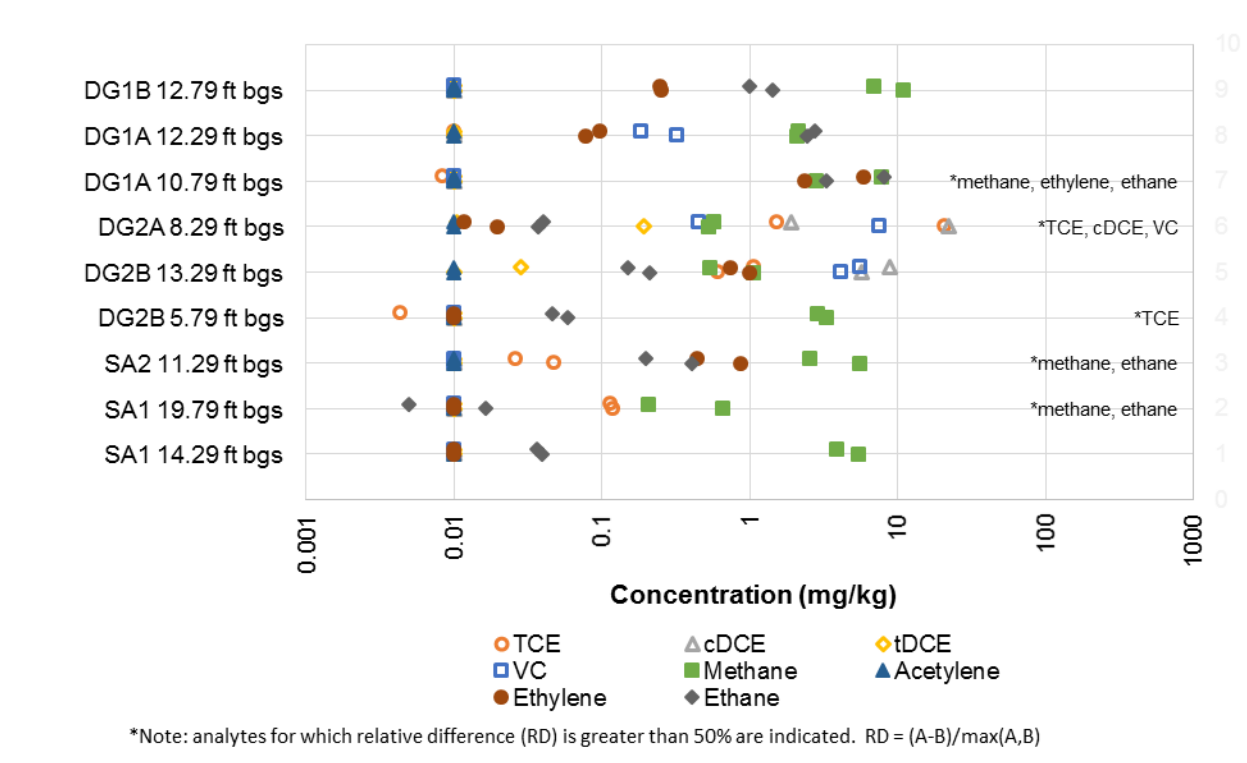
Calibration

With a few exceptions, the analyses were conducted in the laboratory at CSU. Analytical instruments and analyses are described in Section 5.6.2. Calibration standards were prepared and analyzed to generate response factors. Calibration curves were generated using at least five concentrations, bracketing the range of concentrations expected for the field samples.

Quality Assurance Sampling

For frozen soil cores, standard quality assurance (QA) samples such as equipment blanks, trip blanks, and field blanks are not applicable. Duplicate subsamples were collected in the laboratory at a rate of one duplicate per 20 depth-discrete subsamples. Duplicate samples were collected from depths adjacent to the depth of the normal sample. Laboratory blanks were prepared to correspond with each type of laboratory extraction procedure (i.e., methanol- and water-based extraction). In addition, one sample from each core was sent to an external lab for confirmatory analysis.

Results of duplicate sample analyses are presented in the following chart. The duplicate samples are imperfect in that samples represent different sample depths, but the depths are adjacent. For each duplicate sample, analytes for which the relative difference (RD) is greater than 50% are indicated.



Decontamination Procedures

Drilling equipment was decontaminated between each location and before demobilization from the site. Decontamination consisted of steam/pressure washing to remove potentially contaminated soils adhering to drilling equipment and water rinsing. Before the field personnel demobilized from Site 17, Indian Head site personnel provided approval that cleanup procedures were adequate.

Decontamination in the laboratory was conducted in accordance with the high throughput analysis protocol (Sale et al. 2016). Cross-contamination risk is greatly reduced when working with frozen samples. During processing, equipment that contacted the samples, which included the cut-off saw and chisel, was wiped clean of adhering soil particles. A clean sheet of aluminum foil was used as a base during quartering of the frozen sample disks. New out-of-box glassware and high-purity solvents were used for analytical procedures to minimize risk of analytical interference.

Sample Documentation

Upon recovery at the surface, each core segment was inspected, and notes were recorded in a field log book including location, depth, sample time, recovery, and geology. The cores were capped and labeled for location, depth, and orientation (e.g., top and bottom). Packaged cores were placed in coolers with dry ice for shipment. Before shipment, the cooler was sealed with packaging tape. The cooler was sent and received by project team members (Trihydro and/or CSU), so formal chain-of-custody documentation was not required.

Select subsamples were outsourced to an external laboratory for analysis. These subsamples were hand-delivered to a local laboratory (ALS, Fort Collins, Colorado) and included Trihydro chain-of-custody documentation.

APPENDIX G MICROBIOLOGICAL CHARACTERIZATION REPORT

This report presents a summary of methods and results for microbiological analyses conducted as part of this project. Although microbiological characterization was not one of the core analyses conducted in this project, analysis was conducted to supplement geochemical data. Microbiological community preservation presents a potential key advantage to collecting cores cryogenically. At this stage in development, the techniques for microbial extraction and analyses are considered to be works in progress.

Microbiological characterization was conducted using one of the sample quarters generated during processing. Immediately after cutting the core into a frozen disk and quartering, one of the sample quarters was wrapped in aluminum foil and returned to the freezer (-80°C) until DNA extraction. Microbial analysis was performed in triplicate following procedures similar to those described by Irianni-Renno et al. (2016). The samples were pretreated as described by Whitby and Lund (2009), with modifications, to remove potential contaminants (e.g., LNAPL), as described in Irianni-Renno et al. (2016). DNA was quantified via optical density at 260 nm with a Nanodrop™ 2000 reader (Thermoscientific, Wilmington, DE). DNA was extracted in triplicate from each sample and was subsequently stored at -20°C prior to quantitative polymerase chain reaction (qPCR) and next-generation sequencing analysis.

qPCR assays. SYBR™ Green (Life Technologies, Grand Island, NY) qPCR assays were used to quantify the bacterial and archaeal 16S rRNA genes. Genomic DNA extracted *from Desulfovibrio desulfuricans* (ATCC #:27774D-5) and *Methanosarcina acetivorans* (ATCC #: 35395D-5) was used to generate calibration curves for the bacterial and archaeal assays, respectively. The primer sets 27F / 388r and 931AF /1100Ar were used for amplification of bacterial and archaeal 16SrRNA genes, respectively. All assays were performed using an ABI 7300 real-time PCR system (Applied Biosystems, Foster City, CA). Each 25-µl SYBR™Green qPCR reaction included 1X Power SYBR™Green (Life technologies, Grand Island, NY), forward and reverse primers (2.5 µM), magnesium acetate (10 µM), PCR-grade water and 1 ng of DNA template. Thermocycling conditions were as follows: 95˚C for 10 min, followed by 40 cycles of 95˚C for 45 s, 56˚C for 30 s, and 60˚C for 30 s. Dissociation curve analysis was conducted to confirm amplicon specificity.

Next generation sequencing analysis. Sequencing analysis was performed by Research and Testing Laboratories, LLC (Lubbock, TX) using an Illumina MiSeq System (Illumina, San Diego, CA). Community profiling was performed targeting bacterial 16S rRNA genes with primers 28F and 519r and archaeal 16S rRNA genes with primers 517f and 909r.

Data analysis. Results from the microbial communities characterized were evaluated at multiple taxonomic levels. In this report, data are presented at three taxonomic levels (phylum, order and genus) for Bacteria and at two taxonomic levels (phylum and order) for Archaea (Appendix G).

Orders and genera that represent less than 3% of the community are combined with those that are unclassified, and reported as “other.” Phyla that represent less than 0.05% of the community are combined with those that are unclassified and reported as “other.” In addition, when analyzing the bacterial communities at the genus level, organisms that have been shown to share functional capabilities, such as putative sulfate reducers, iron reducers, and methane oxidizers, were reported in the following groups:

- Putative sulfate reducers included organisms belonging to the following genera: *Desulfotomaculum* spp., *Thermodesulfovibrio* spp., *Desulfatirhabdium* spp., *Desulfobacterium* spp, *Desulfobulbus* spp. *Desulfocella* spp., Unclassified *Desulfobacteraceae*, *Desulfovibrio* spp., *Desulfobacca* spp., *Desulfomonile* spp., *Desulfovirga* spp., *Desulfuromonas* spp., *Thermodesulfobacterium* spp.
- Putative iron reducers included organisms belonging to the following genera: *Rhodoferax* spp., *Geobacter* spp., *Geothermobacter* spp.
- Putative methane oxidizers included organisms belonging to the following genera: *Methylocapsa* spp., *Methylocella* spp., *Methylobacterium* spp., *Methylocystis* spp., *Methylosinus* spp., *Methylobacillus* spp., Unknown *Methylophilaceae*.

Results. Results are shown below for each of the six soil-coring locations.

Location SA1

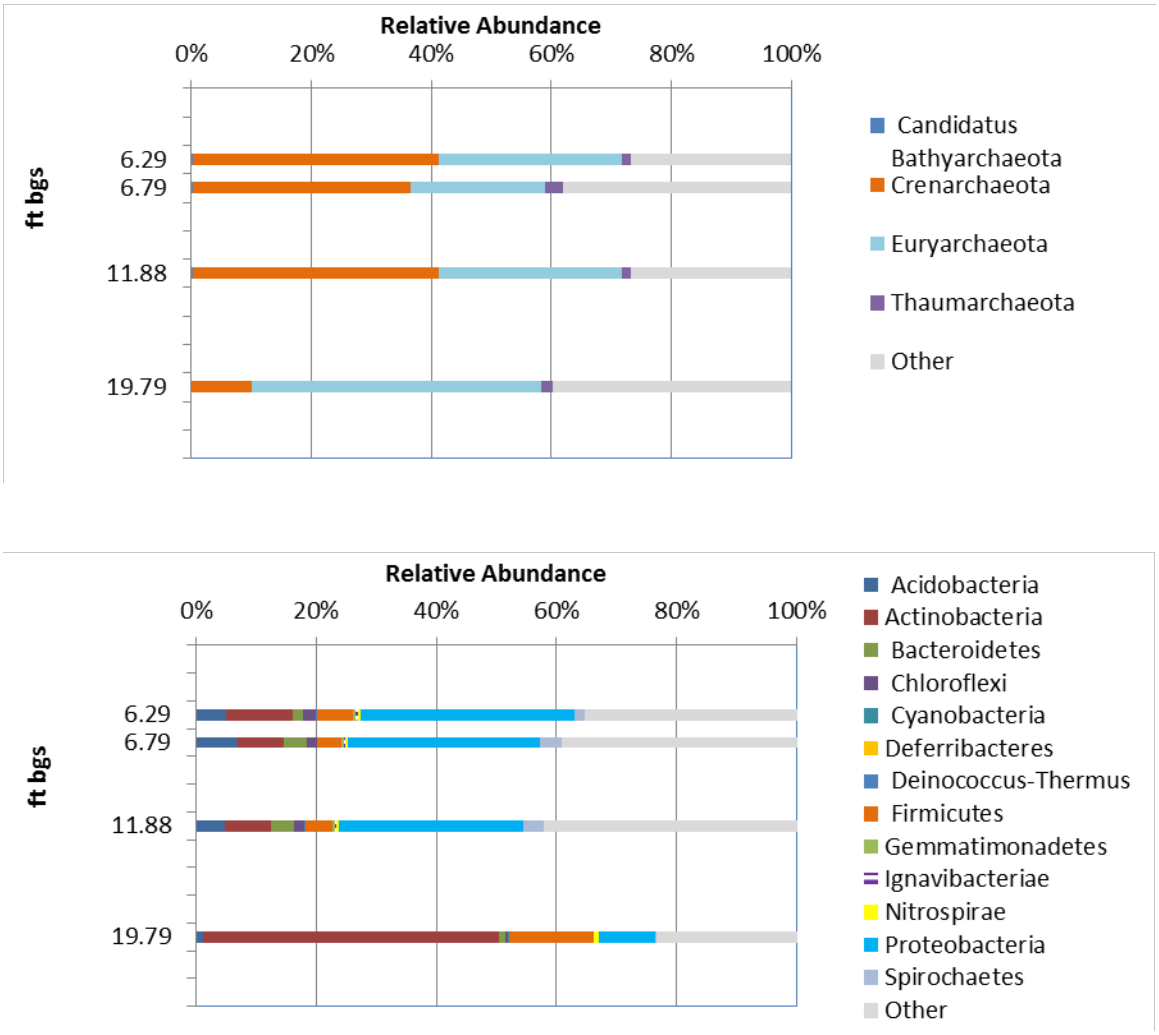


Figure Error! Reference source not found.**-1: Archaeal (upper) and Bacterial (lower) Community Composition of Subsamples Collected from Core SA1: PhylumLlevel.**

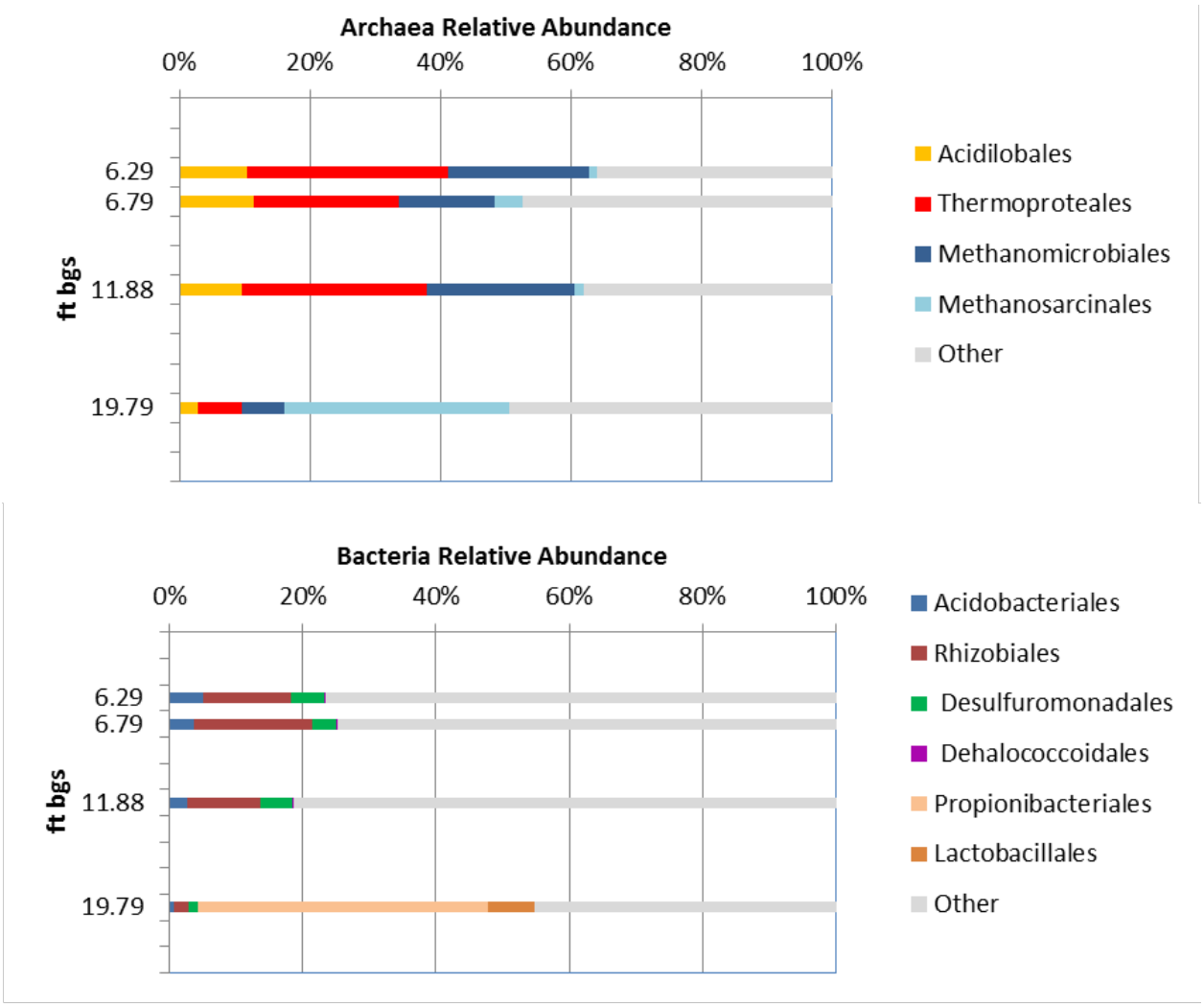


Figure Error! Reference source not found.**-2: Archaeal and Bacterial Community Composition of Subsamples Collected from Core SA1: Order Level.**

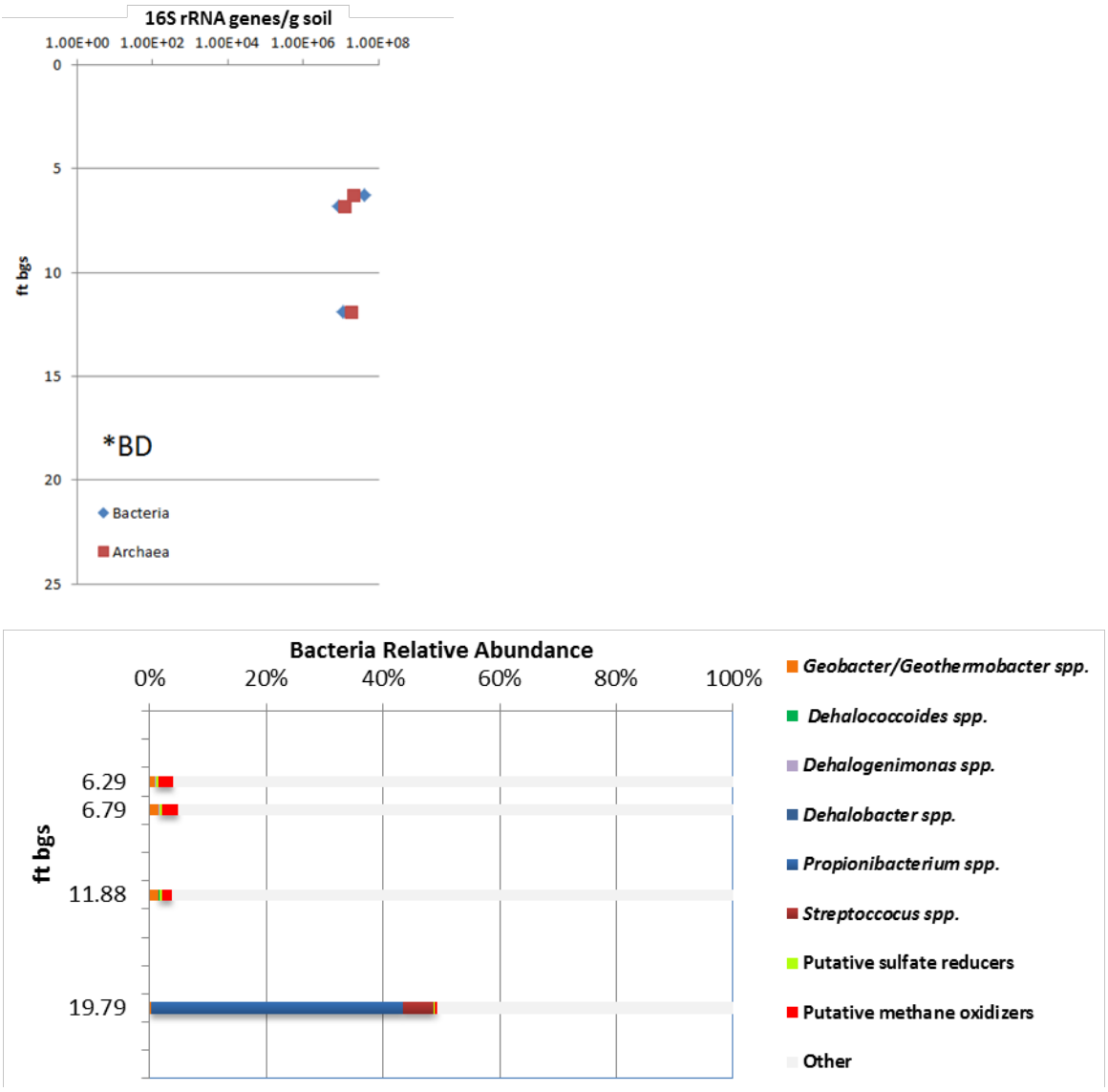


Figure Error! Reference source not found.**-3: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core SA1: Genus Level.**

No Bacteria or Archaea were detected in qPCR analysis of the sample collected at 19.78 ft bgs.

- The samples collected at 6.29 and 6.79 ft bgs had insignificant numbers of dechlorinators present. Putative methane oxidizers were identified (red) in these samples. Approximately between 16 and 19% of the archaeal community was identified as methanogens (Fig. G-2).
- The sample collected at 11.88 ft bgs contained insignificant numbers of dechlorinators. Methane oxidizers were present. Approximately 1.5% of the bacterial community was identified as putative iron reducers belonging to the genera *Geobacter* or *Thermogeobacter*.
- The sample collected at 19.79 ft bgs yielded very low amounts of DNA. Both bacterial and archaeal 16S rRNA genes were below detection limit when quantified via qPCR. Sample sequencing was only successful for bacterial genes.

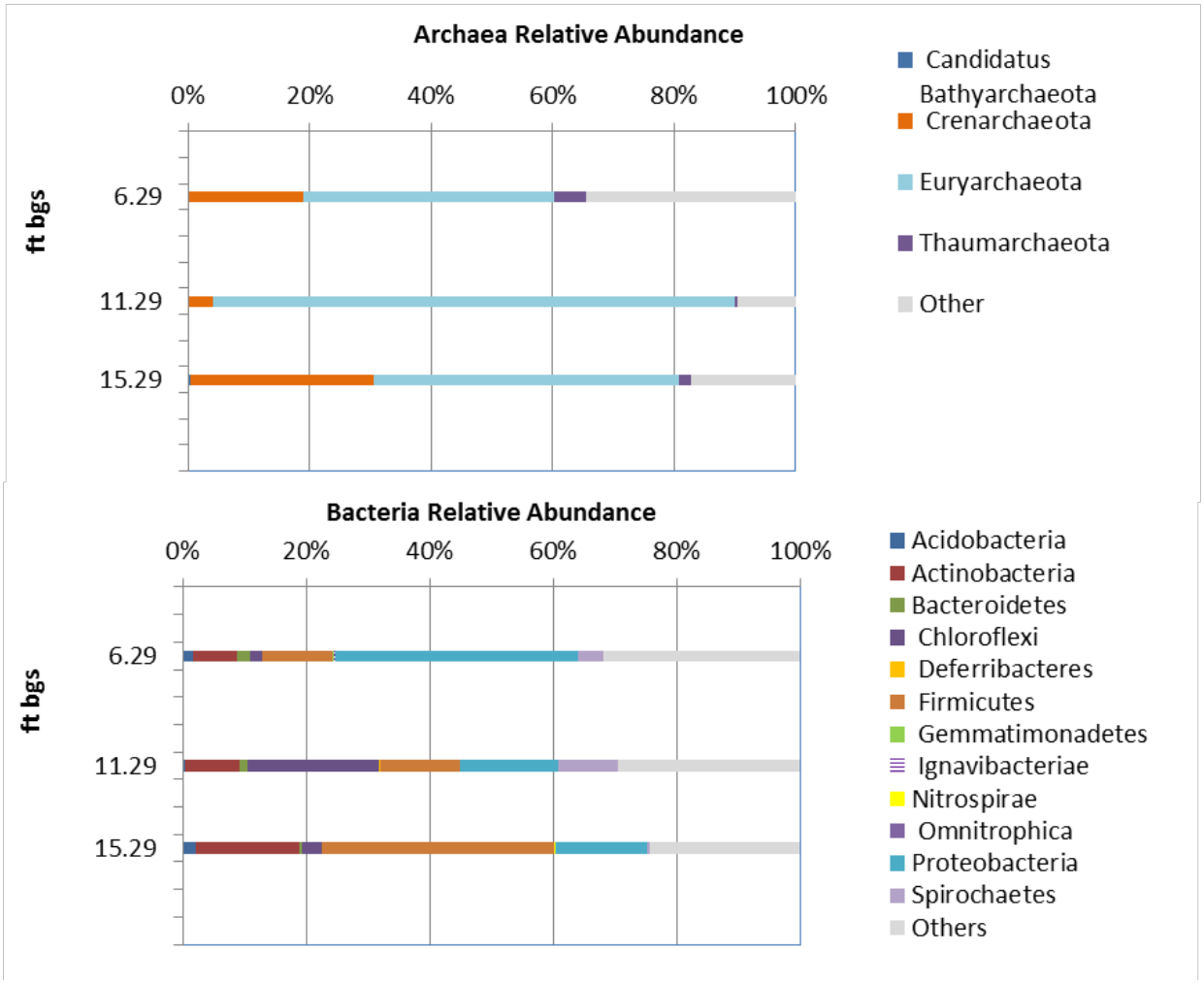


Figure Error! Reference source not found.**-4: Archaeal and Bacterial Community Composition of Subsamples Collected from Core SA2: Phylum Level.**

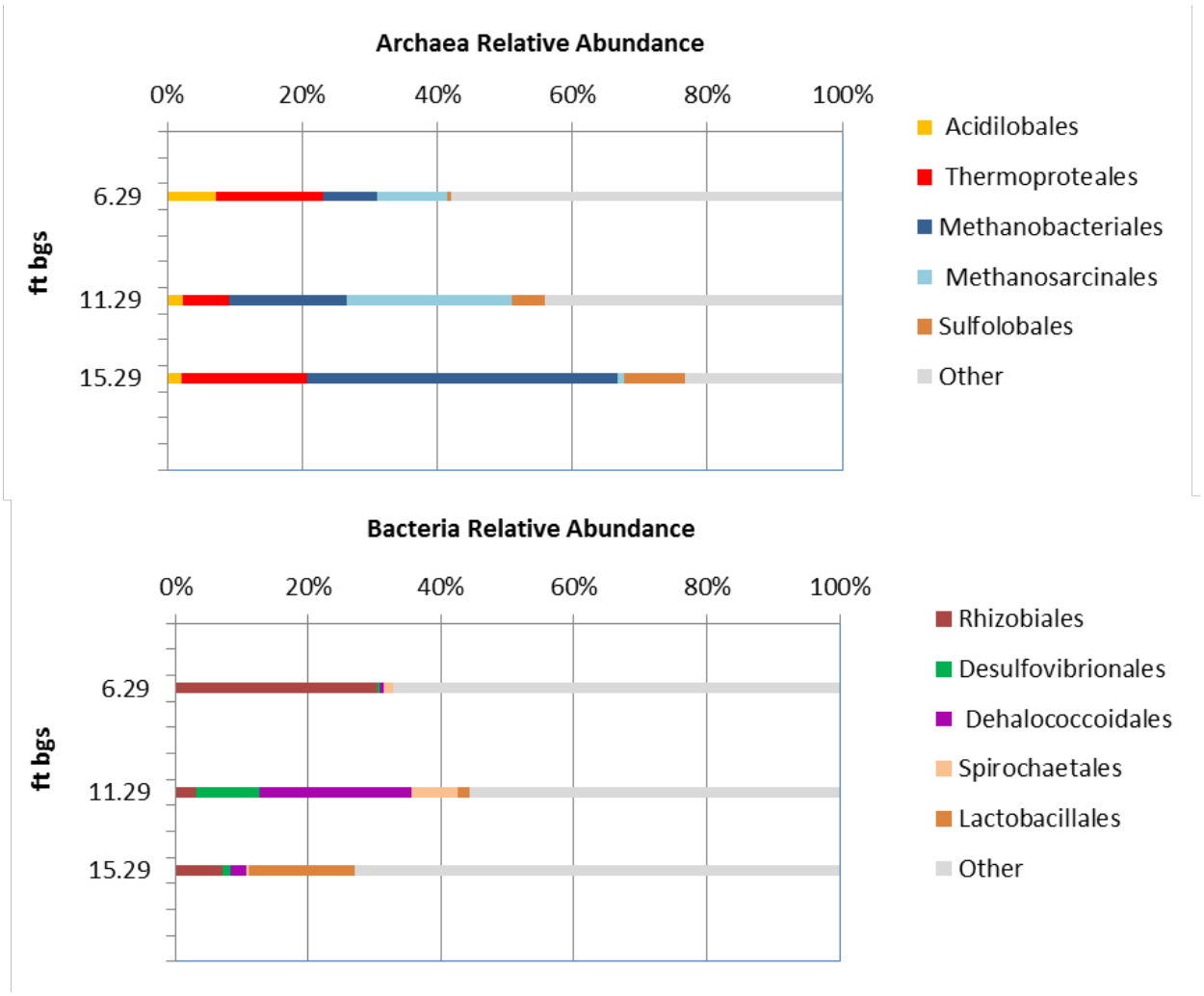


Figure Error! Reference source not found.**-5: Archaeal and Bacterial Community Composition of Subsamples Collected from Core SA2: Order Level.**

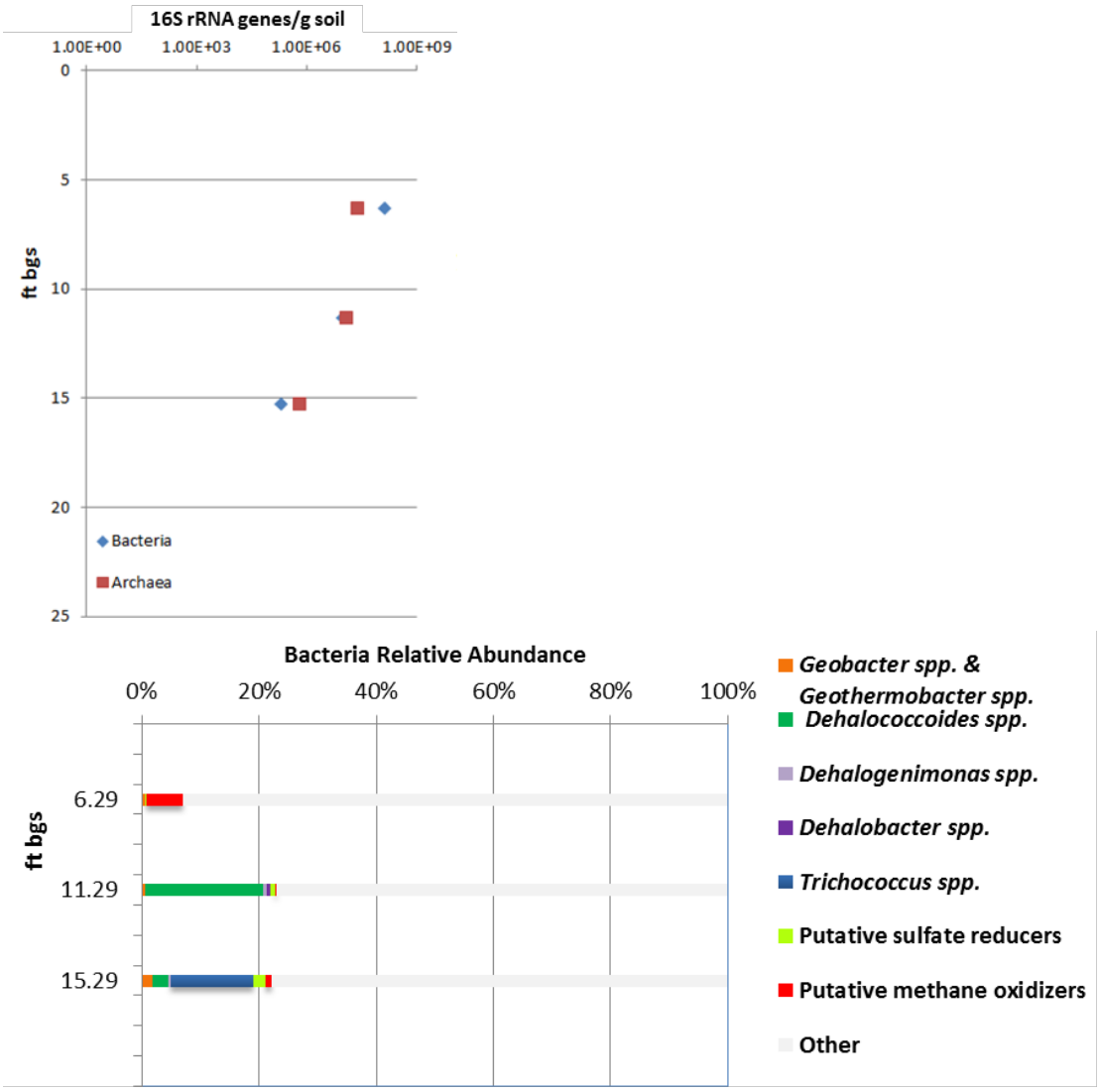


Figure Error! Reference source not found.**-6: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core SA2: Genus Level.**

- Insignificant amounts of dechlorinators and putative iron reducers were found in the sample collected at 6.29 ft bgs. This sample had relatively high organic content (almost 3% by weight). Approximately 40% of the archaeal community of this sample corresponds to putative methanogens (Fig. G-5).
- The sample collected at 11.29 ft bgs contained significant numbers of putative dechlorinators belonging to the genus *Dehalococcoides* (20.1%); this finding is consistent with high levels of cis-DCE and ethylene measured in the sample. Approximately 73.2% of the archaeal community was identified as methanogenic, which is consistent with the higher methane concentrations measured in this sample.
- The sample collected at 15.29 ft bgs contained some dechlorinators (2.7%). Part of the bacterial community (14%) was identified as members of the genus *Trichococcus.* 1.5% of the sequenced bacterial community belonged to either the genera *Thermogeobacter* or *Geobacter*.

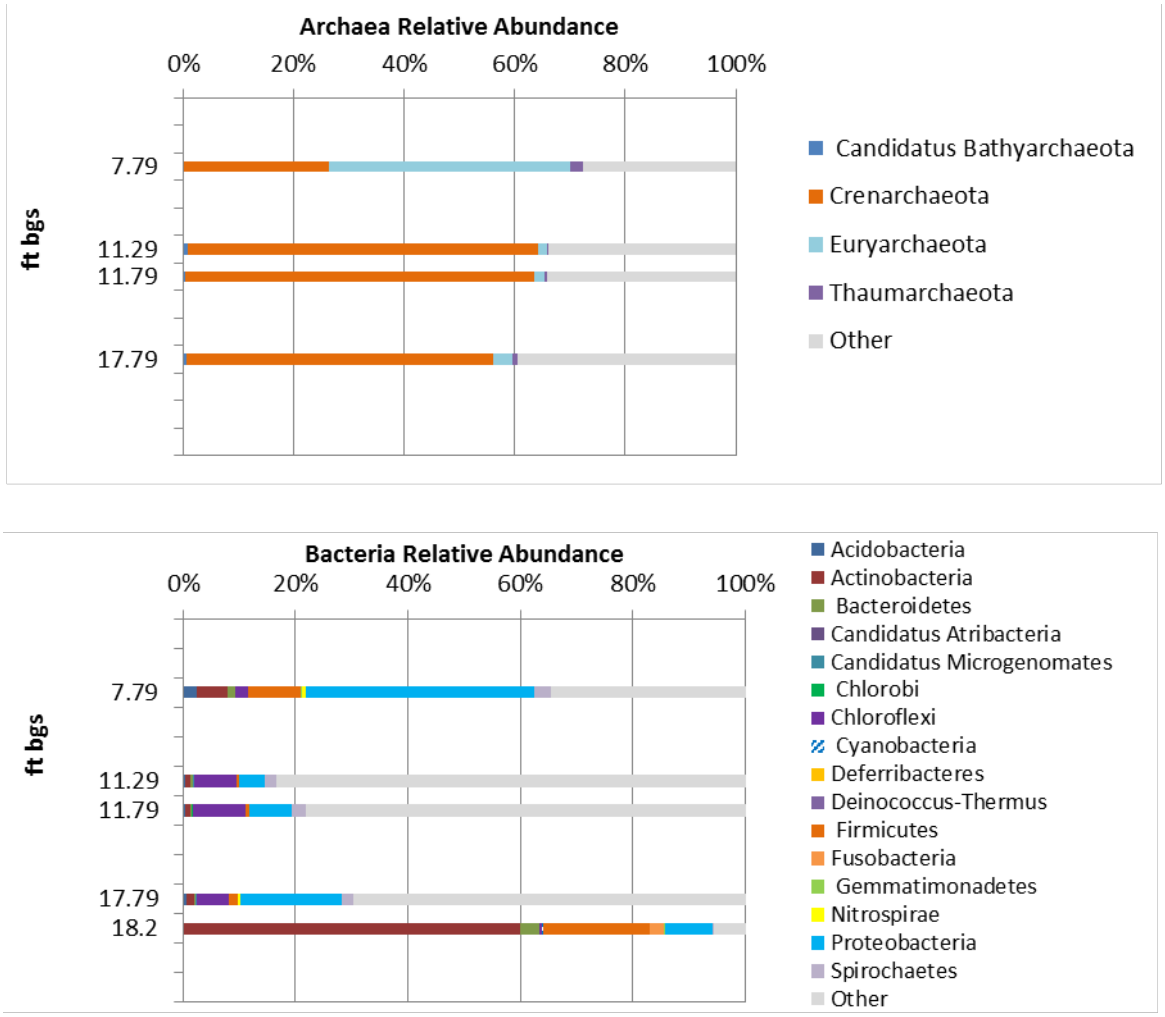


Figure Error! Reference source not found.**-7: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1A: Phylum Level.**

The sample collected at 18.2 ft bgs yielded no archaeal results.

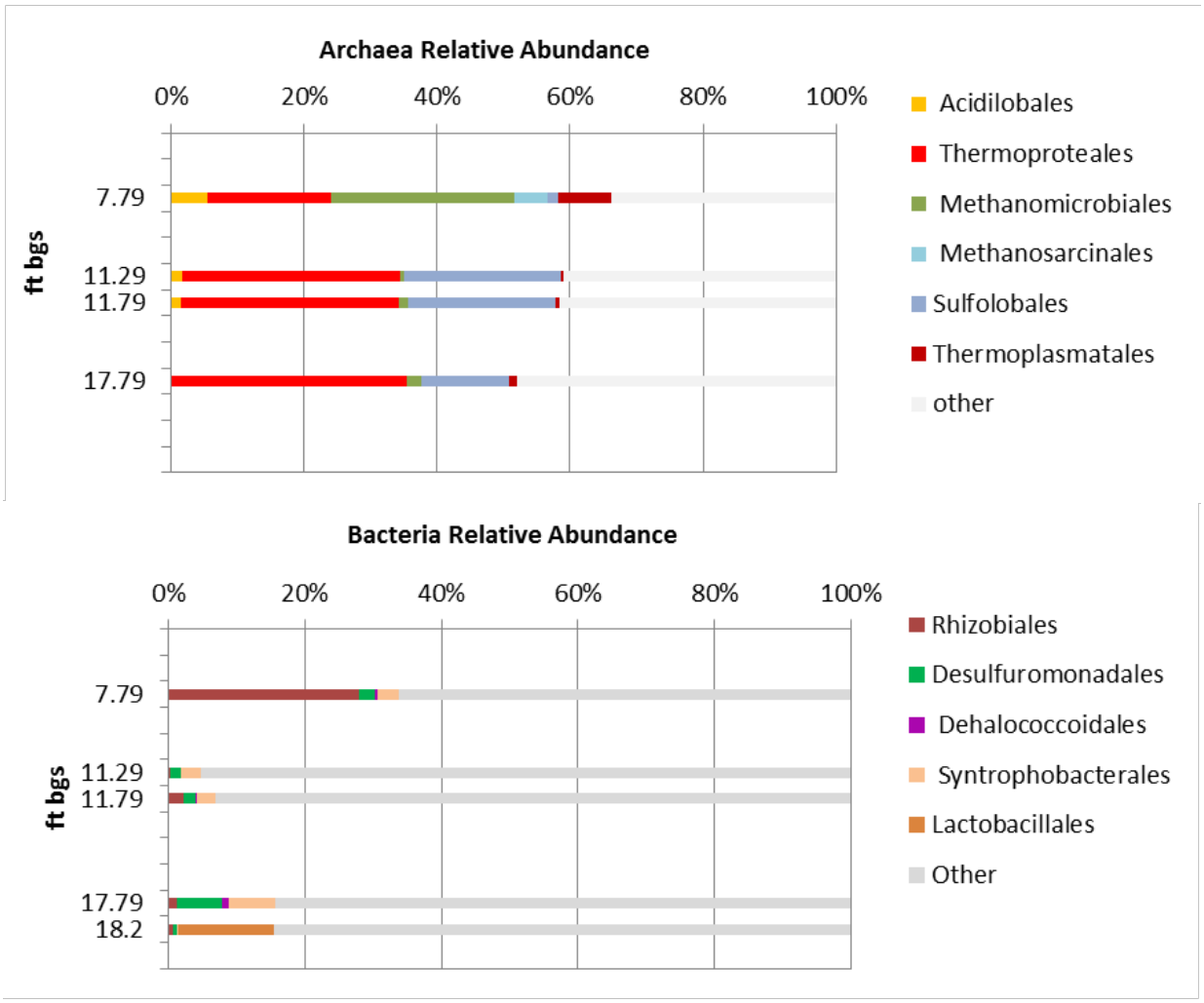


Figure Error! Reference source not found.**-8: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1A: Order Level.**

The sample collected at 18.2 ft bgs yielded no archaeal results.

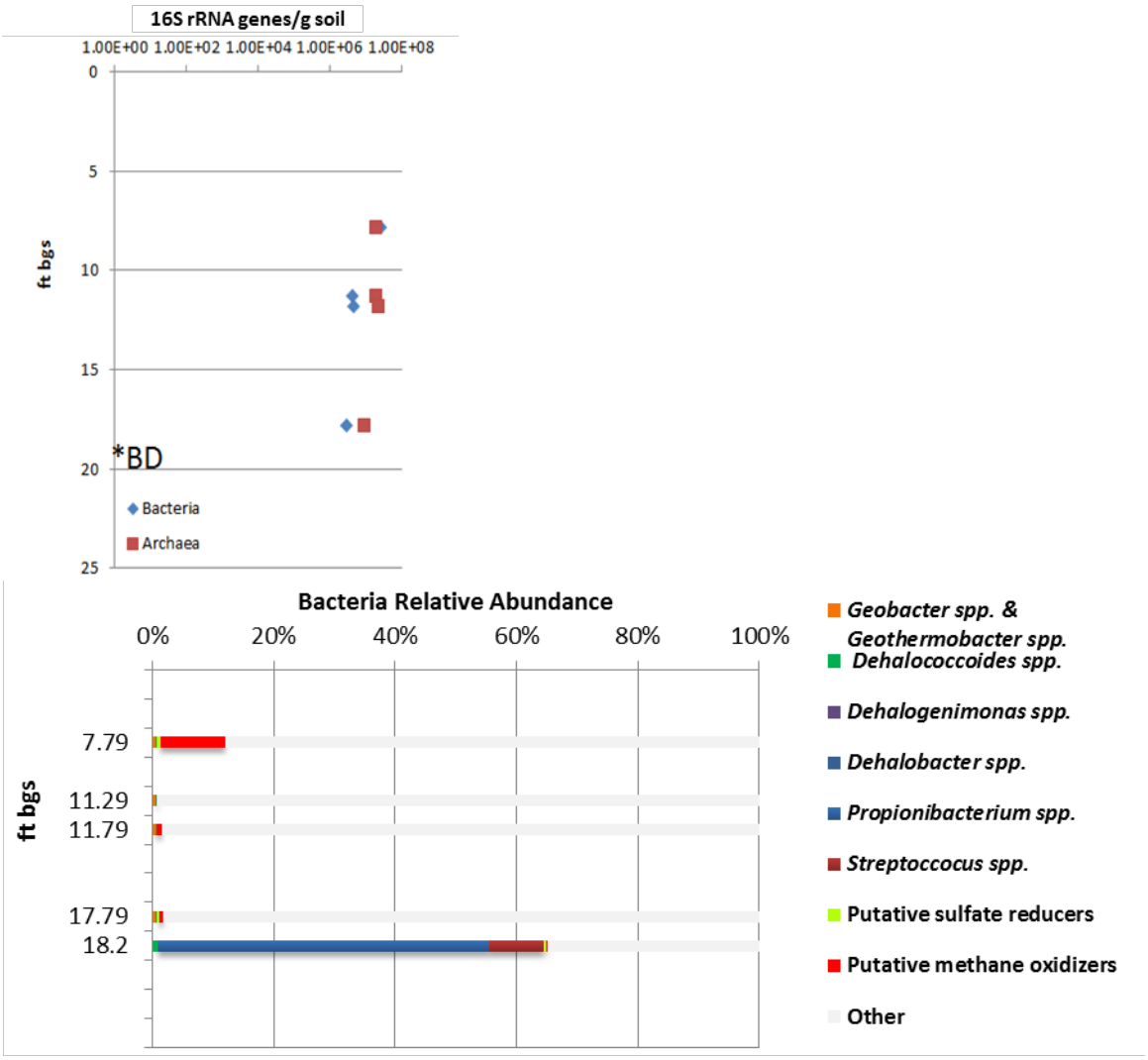


Figure Error! Reference source not found.**-9: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG1A: Genus Level.**

No Bacteria or Archaea were detected in qPCR analysis of the sample collected at 18.2 ft bgs.

- The sample collected at 7.79 ft bgs contained some putative methane oxidizers. Approximately 32% of the archaeal community was identified as methanogens (Fig. G-8).

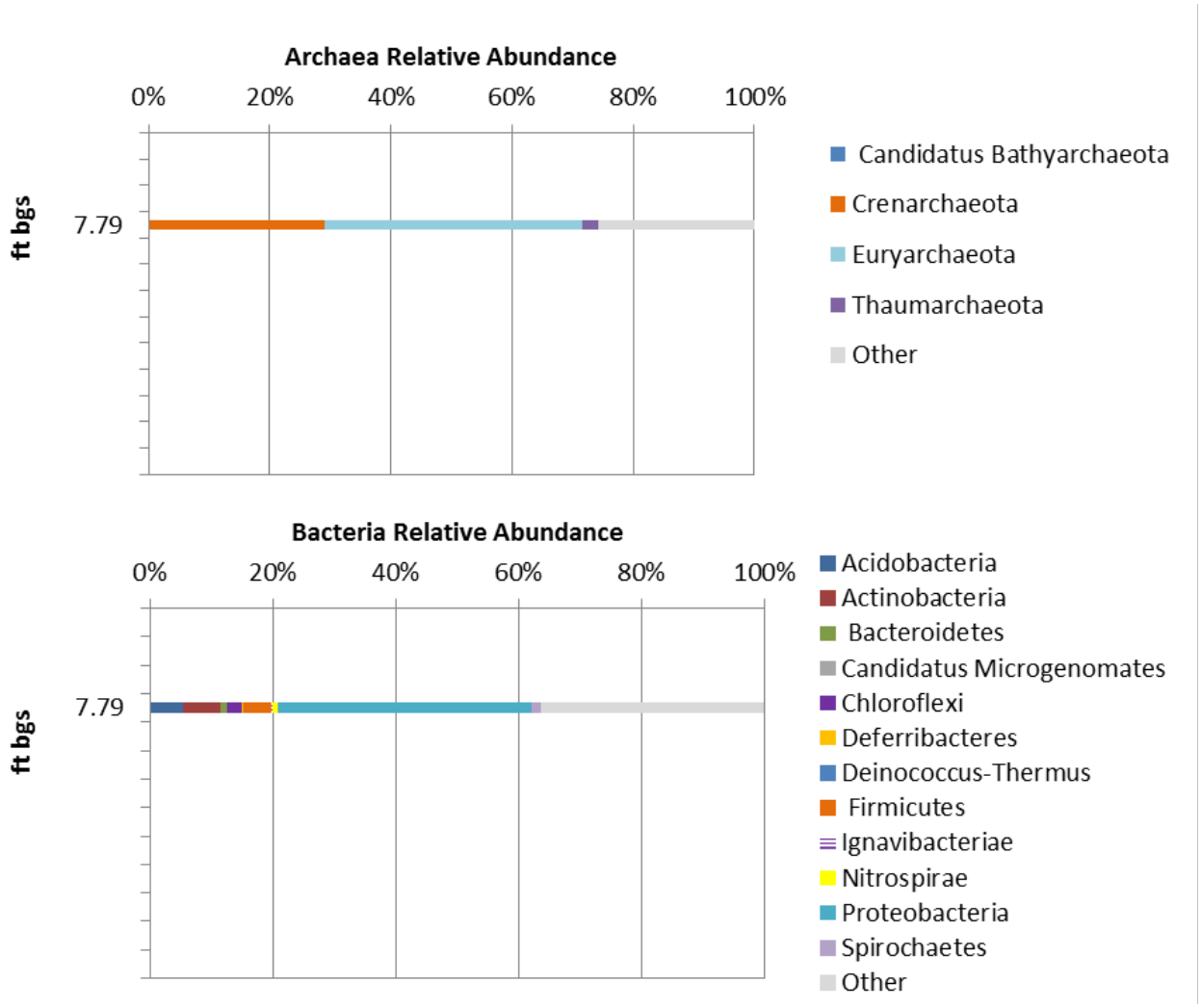


Figure Error! Reference source not found.**-10: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1B: Phylum Level.**

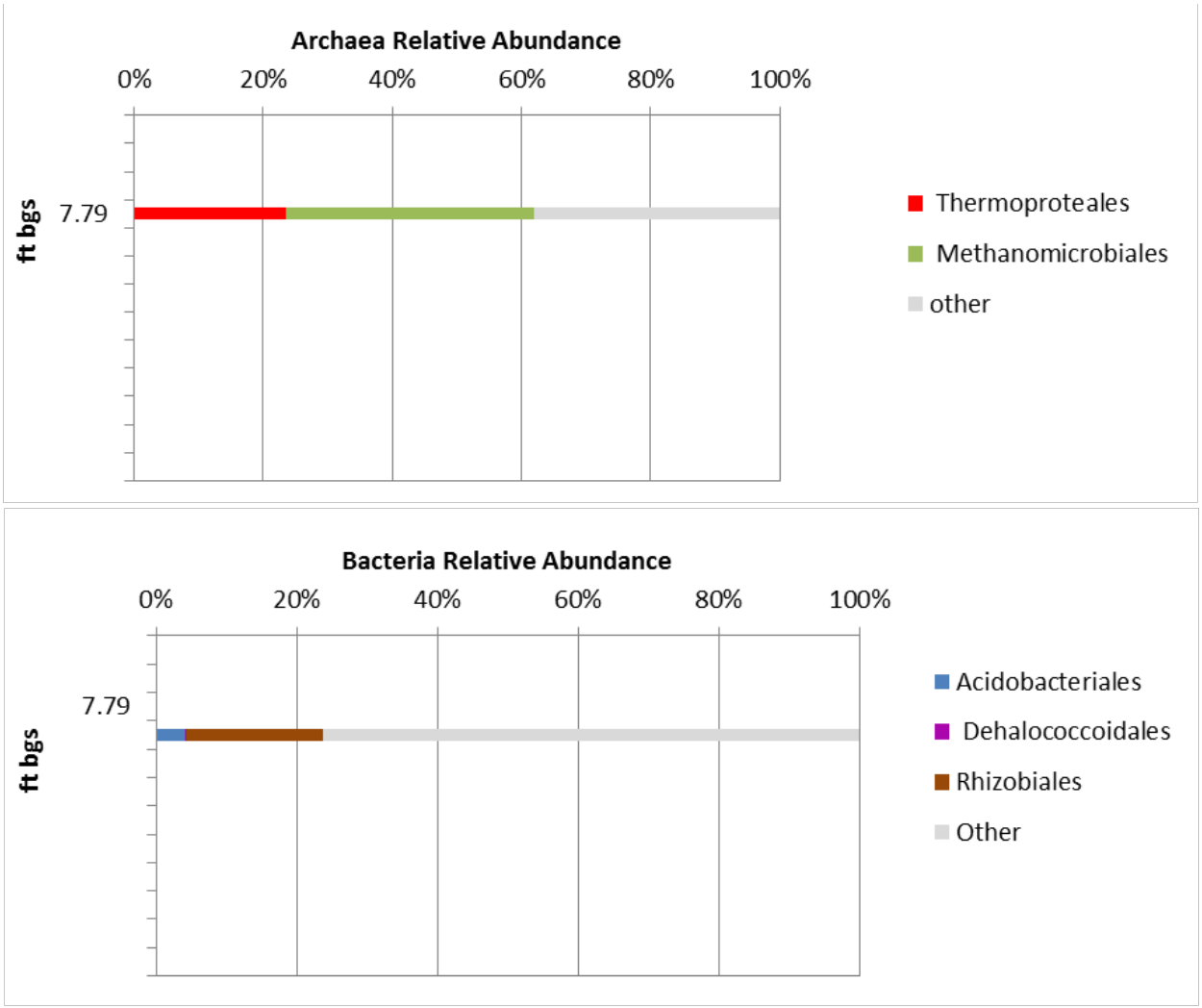


Figure Error! Reference source not found.**-11: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1B: Order Level.**

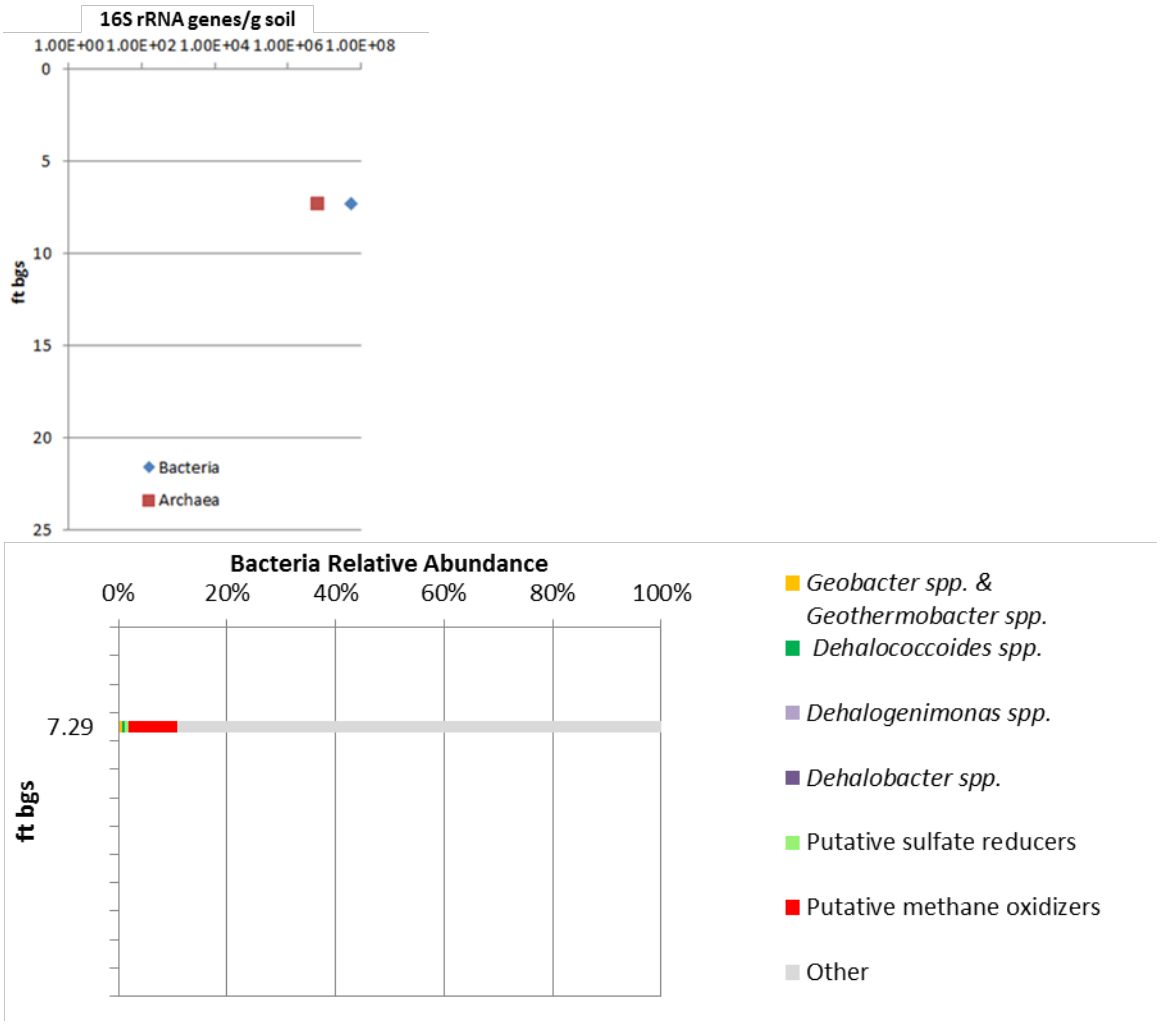


Figure Error! Reference source not found.**-12: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG1B: Genus Level.**

- No significant numbers of dechlorinators were found in this sample. Methane oxidizers were present. Approximately 31% of the archaeal community was identified as methanogens (Fig. G11).

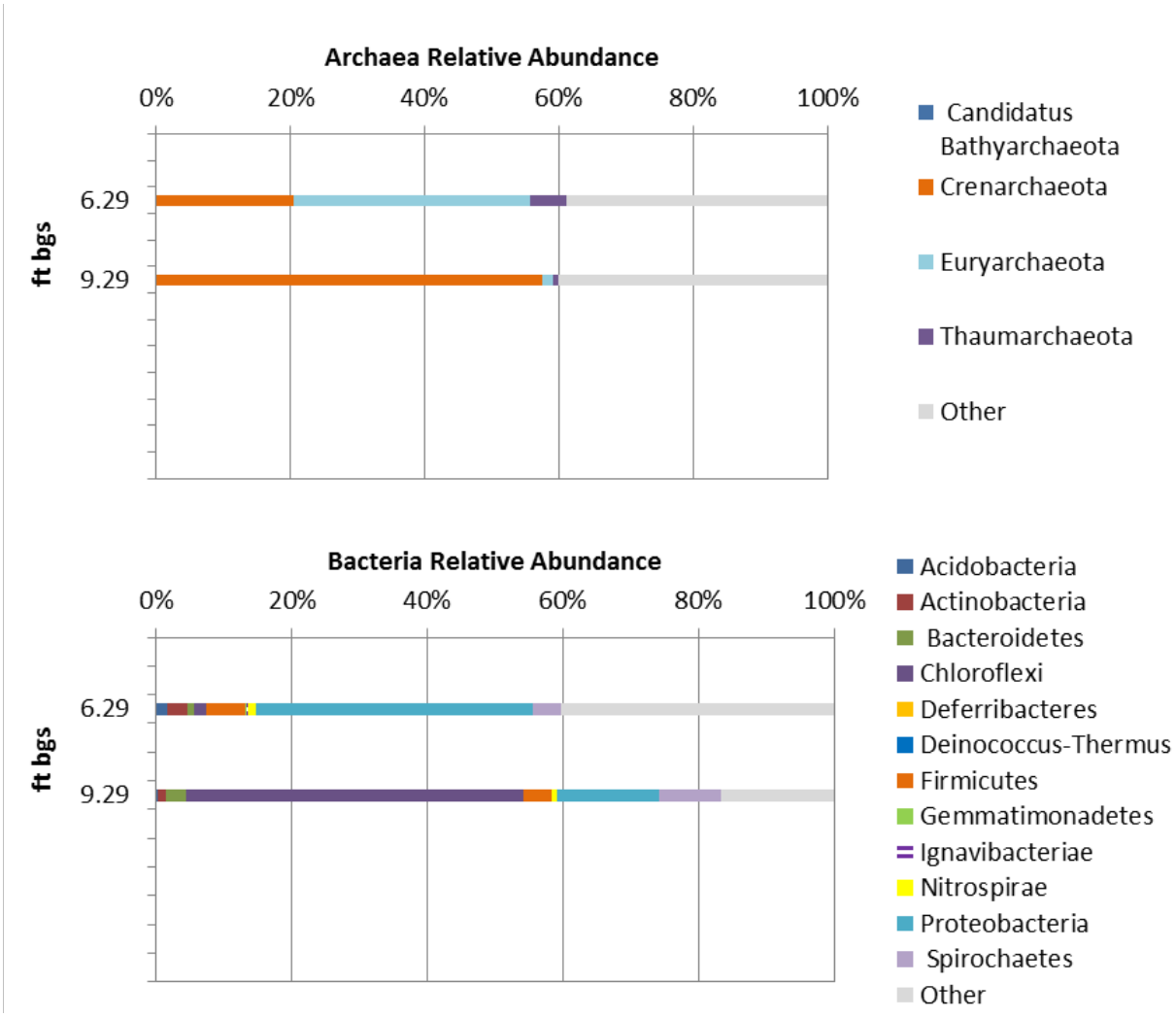


Figure Error! Reference source not found.**-13: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2A: Phylum Level.**

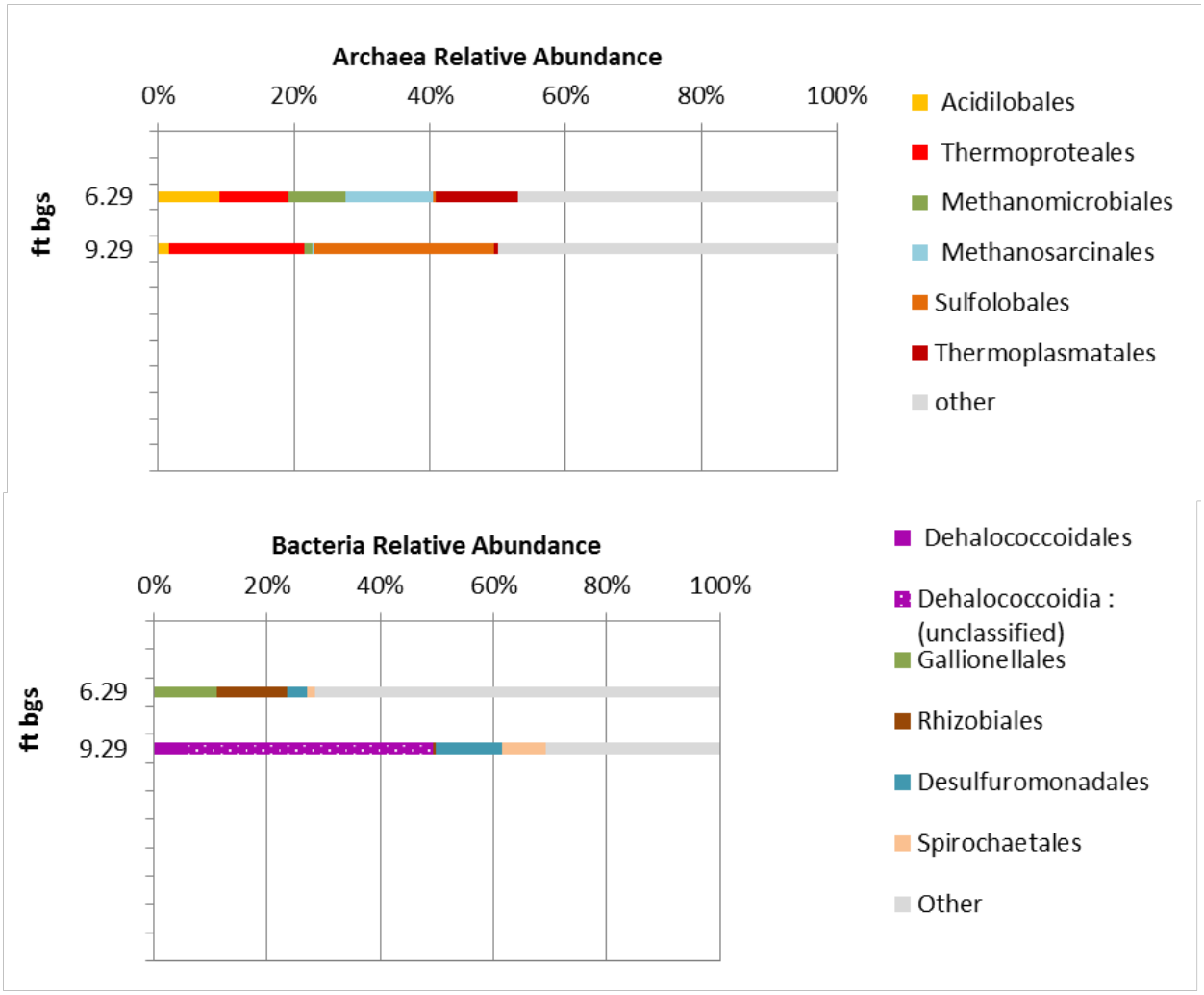


Figure Error! Reference source not found.**-14: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2A: Order Level.**

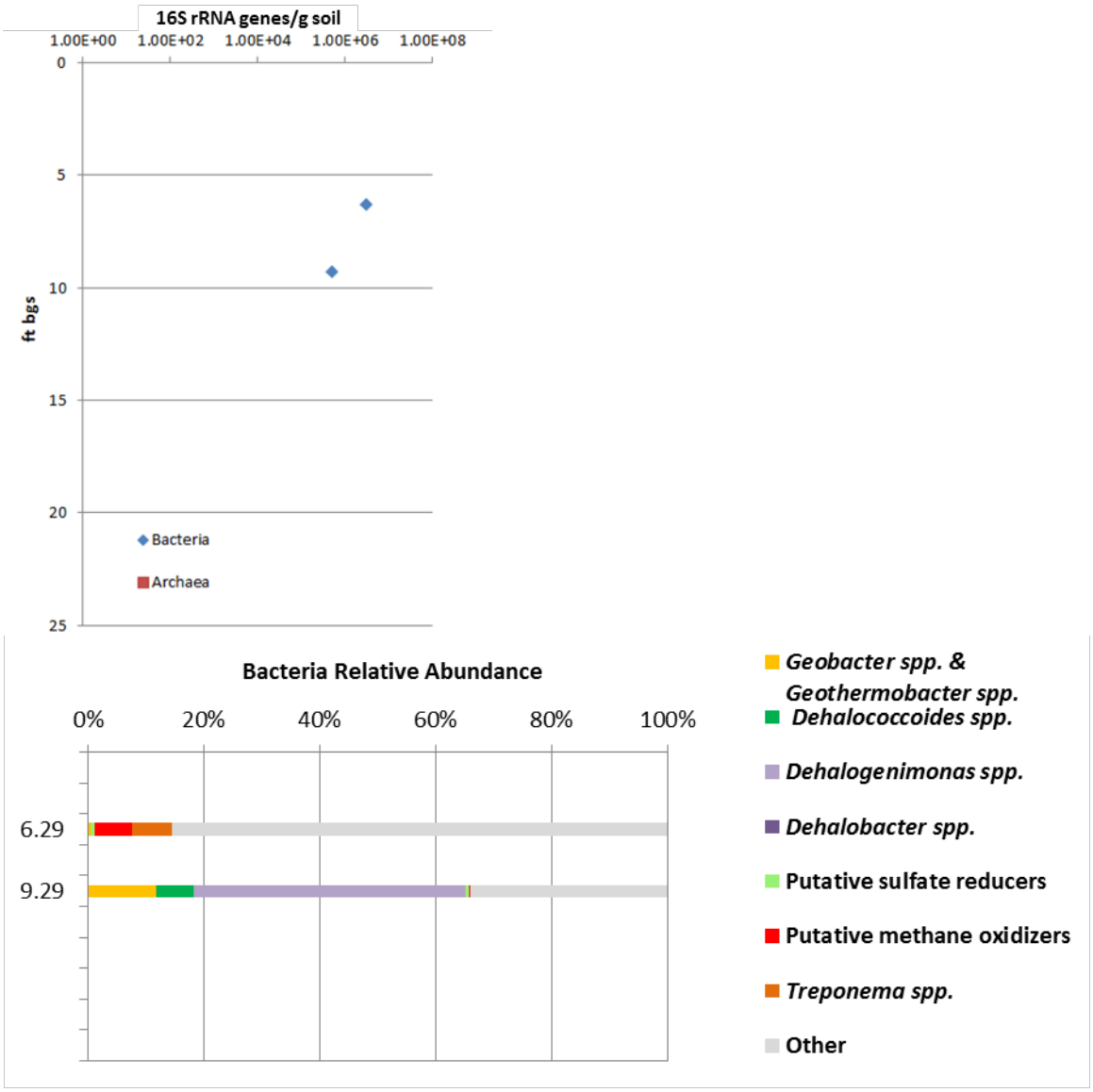


Figure Error! Reference source not found.**-15: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG2A: Genus Level.**

No Archaea were detected in qPCR analysis of either sample analyzed from core DG2A.

No Archaea were detected through qPCR. For the sample collected at 9.29 ft bgs, 43% of the characterized bacterial community belonged to the genus *Dehalogenimonas*. Some members of this genus have been identified as able to grow by organohalide respiration, coupling the oxidation of H_2 to the reductive dehalogenation of polychlorinated alkanes. Additionally, 6% of the characterized bacteria within this sample belonged to the genus *Dehalococcoides*. Ethylene and *c*DCE were present in this sample. A substantial part of the bacterial community was identified as putative iron reducers. 11 % of the characterized bacterial community belongs to either the genus *Geobacter* or to the genus *Thermogeobacter*. Relative to other analyzed samples, large amounts of ferrous iron were detected within this sample.

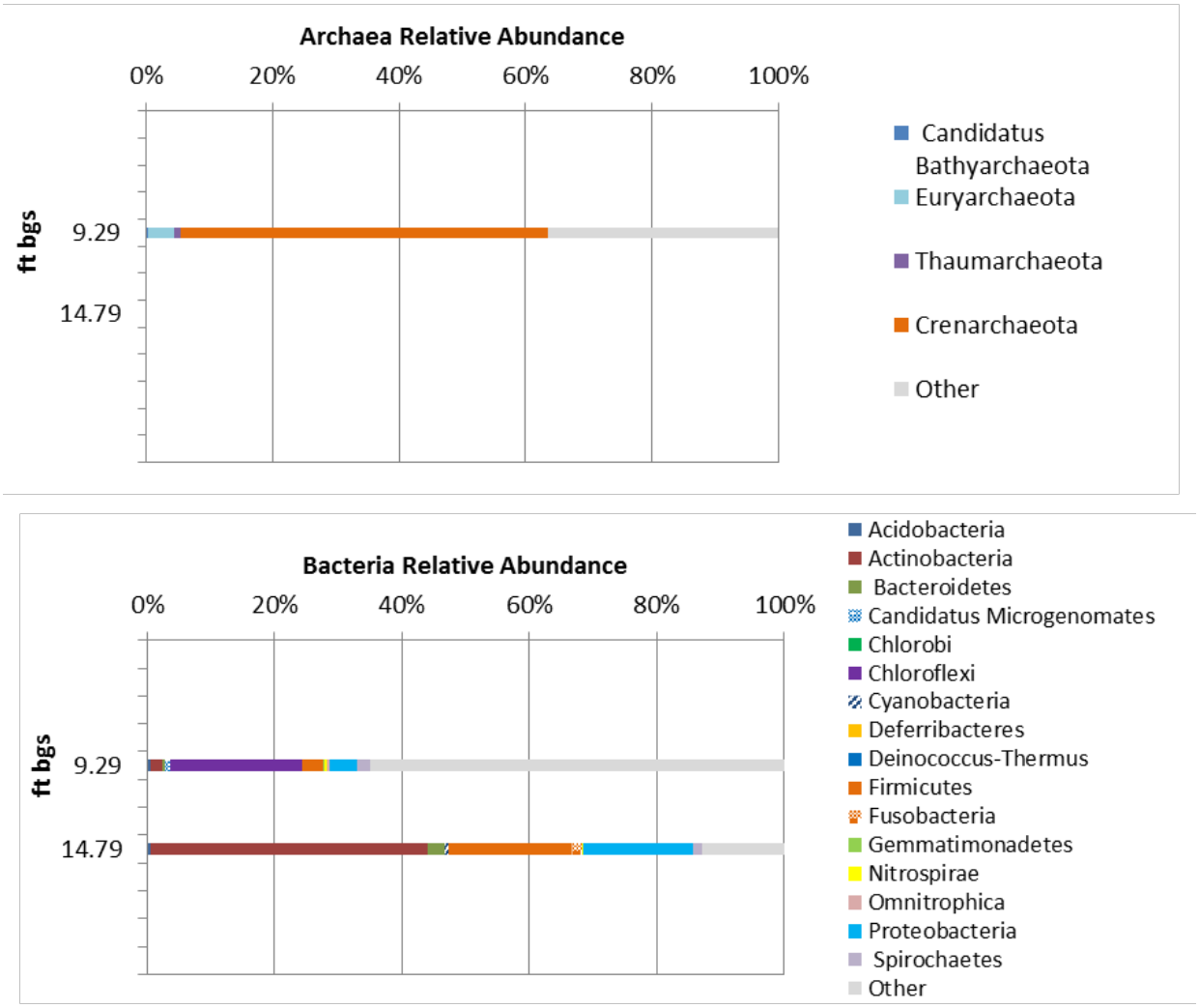


Figure Error! Reference source not found.**-16: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2B: Phylum Level.**

No Archaea were detected at 14.79 ft bgs, via sequencing analysis of the archaeal 16S rRNA gene.

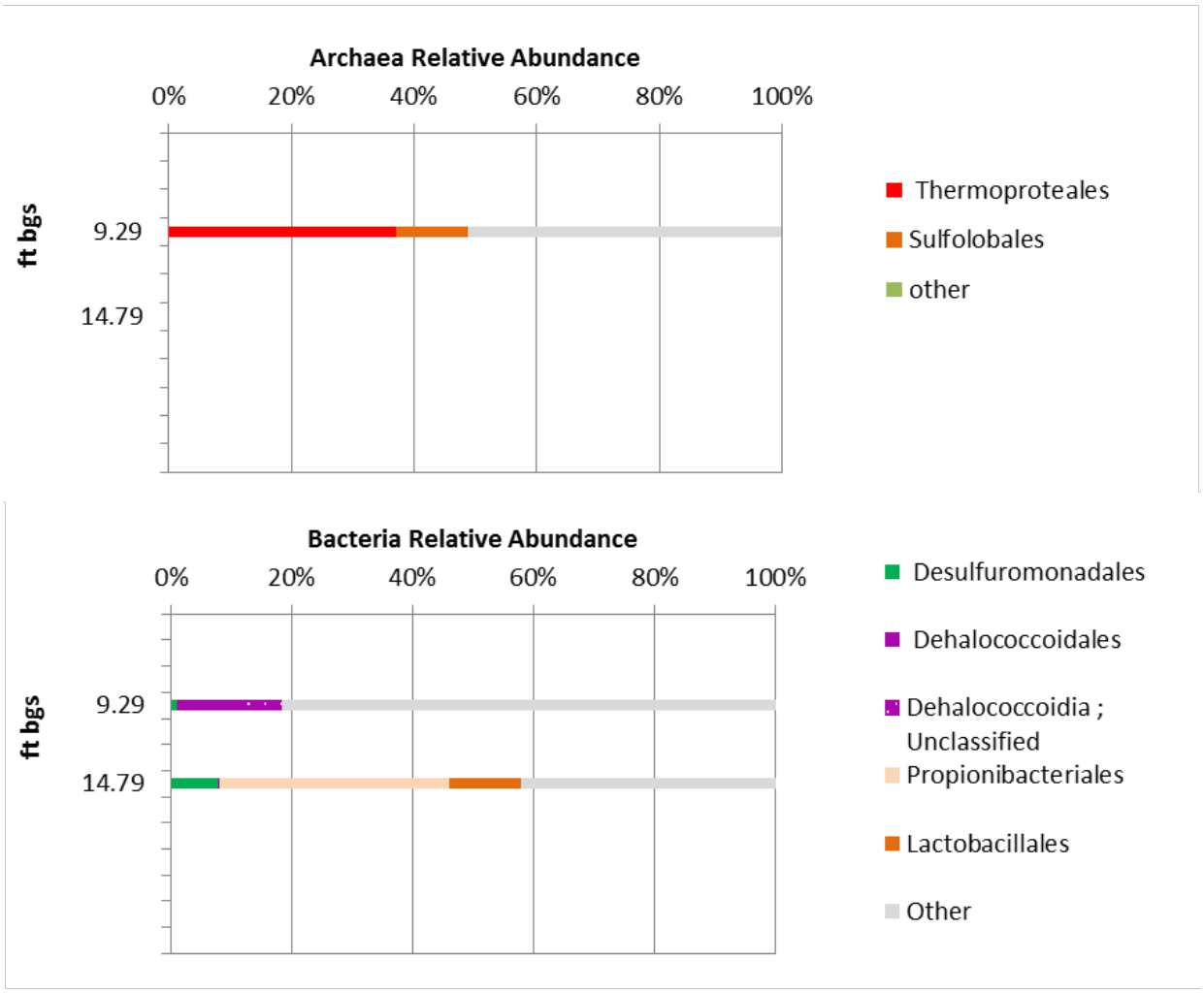


Figure Error! Reference source not found.**-17: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2B: Order Level.**

No Archaea were detected at 14.79 ft bgs, via sequencing analysis of the archaeal 16S rRNA gene.

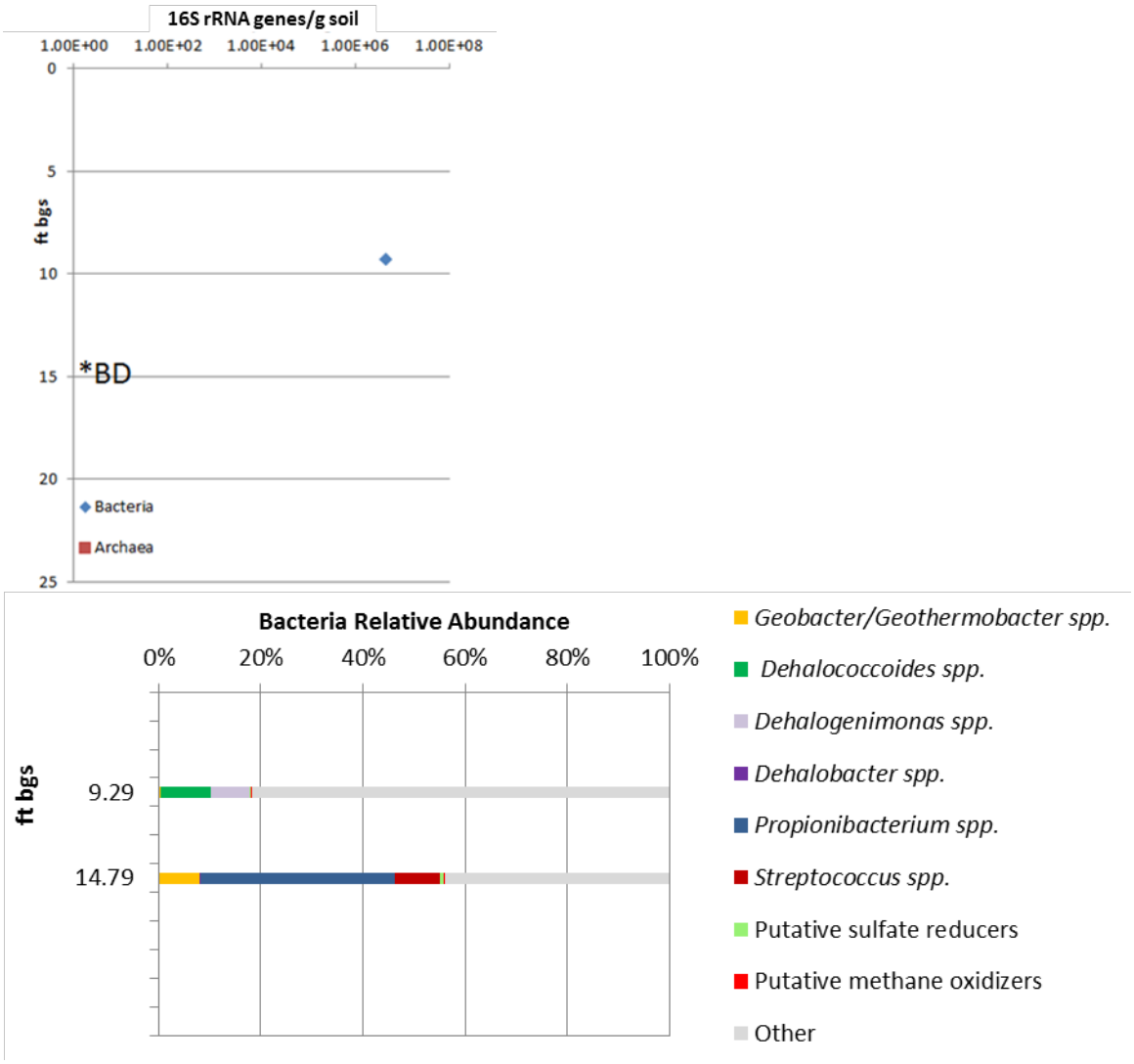


Figure Error! Reference source not found.**-18: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG2B: Genus Level.**

No Archaea were detected in qPCR analysis of either sample analyzed from core DG2B and no Bacteria were detected in qPCR analysis of the sample collected at 14.79 bgs.

No Archaea were detected through qPCR in either of the samples presented above. Sequencing of the archaeal 16S rRNA genes yielded no results. Approximately 9.9% of the characterized bacterial community analyzed for the sample collected at 9.29 ft bgs belonged to the genus *Dehalogenimonas*. 7.5% of the characterized bacteria within this sample belonged to the genus *Dehalococcoides*. Ethylene and *c*DCE were present in this sample as well.

Subsamples collected at 13.79, 14.29, 15.79 and 18.79 ft bgs were also analyzed from this core, but little or no DNA was recovered. Therefore, no downstream sample analysis was possible.

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APPENDIX H TABULATED C_3 DATA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
75	SA1	3.29	0	0.29	0.12	0	ND	15	ND	ND	0	NA	ND	NA	NA	NA	NA	3	NA
74	SA1	3.79	ND	0.13	ND	ND	ND	6.7	ND	ND	0	1.9	3.8	240	15	350	NA	3	NA
73	SA1	4.29	0.1	0.15	0.08	ND	ND	3.4	ND	ND	ND	NA	NA	NA	NA	NA	NA	2.4	NA
79	SA1	6.29	0	0.29	ND	ND	ND	21	ND	ND	0	1.9	3.9	220	10	760	NA	2.9	NA
78	SA1	6.79	ND	0.2	0.17	ND	ND	7.8	ND	ND	0	1.9	10	150	6.6	92	0.9	3	ND
80	SA1	11.88	ND	0.17	ND	ND	ND	14	ND	ND	0	1.9	2.1	170	11	540	NA	3.2	NA
82	SA1	14.21	ND	ND	ND	ND	ND	3.8	ND	ND	0	NA	NA	NA	NA	NA	NA	3.2	NA
81	SA1	14.29	ND	ND	ND	ND	ND	5.4	ND	ND	0	1.9	2.6	170	12	120	NA	3	NA
83	SA1	16.79	ND	ND	ND	ND	ND	8.7	ND	ND	0.1	6.5	18	220	13	37	0.2	3	NA
85	SA1	18.79	ND	ND	ND	ND	ND	5.7	ND	ND	0.1	4.7	15	200	13	69	NA	3	NA
84	SA1	19.29	ND	0.02	ND	ND	ND	1.6	ND	ND	0	4.7	3.6	180	27	150	NA	3.2	NA
91	SA1	19.71	ND	0.11	ND	ND	ND	0.2	ND	ND	0	1.9	ND	110	7.4	540	0.4	3	NA
90	SA1	19.79	ND	0.12	ND	ND	ND	0.7	ND	ND	0	1.9	ND	120	9.2	570	NA	3	NA
89	SA1	20.29	ND	0.23	0.06	ND	ND	1	ND	ND	0	1.9	ND	130	9.5	470	NA	3	NA
88	SA1	20.79	ND	0.45	0.27	ND	ND	0.5	ND	ND	0	1.9	ND	200	8.9	720	NA	2.9	NA
87	SA1	21.29	ND	0.53	0.15	ND	ND	0.3	ND	ND	0	1.9	ND	230	6.9	480	NA	3	ND
86	SA1	21.79	ND	0.48	0.21	ND	ND	0.2	ND	ND	ND	1.9	ND	290	10	470	0.4	2.9	NA
94	SA2	3.29	ND	0.07	0.85	0	ND	4.4	ND	ND	0	1.9	ND	790	13	470	NA	2.9	NA
93	SA2	3.79	ND	0.14	0.35	ND	ND	13	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	NA
92	SA2	4.29	ND	0.07	ND	0	ND	8.6	ND	ND	0.1	30	31	900	9.8	33	NA	3	NA
96	SA2	6.29	ND	ND	0.15	ND	ND	4.2	ND	ND	0	NA	NA	NA	NA	NA	NA	3	NA
95	SA2	6.79	ND	0.17	0.29	ND	0.1	6.1	ND	ND	0.1	1.9	ND	34	ND	11	2.8	3.1	NA
98	SA2	9.04	ND	0.08	0.2	ND	ND	8.6	ND	0	0.2	1.9	ND	1100	4.7	400	NA	3	NA
97	SA2	9.29	ND	0.05	ND	ND	ND	9.2	ND	ND	0.4	NA	NA	NA	NA	NA	NA	3.1	NA
101	SA2	11.21	ND	0.03	ND	ND	ND	2.5	ND	0.4	0.2	NA	NA	NA	NA	NA	NA	3.1	NA
100	SA2	11.29	ND	0.05	ND	ND	ND	5.6	ND	0.9	0.4	48	ND	3300	12	40	NA	3	NA
99	SA2	11.79	ND	ND	ND	ND	ND	8.1	ND	1.4	0.7	3	2.6	2100	3.5	150	0.3	3.2	NA
103	SA2	13.79	ND	0.04	ND	ND	ND	5.4	ND	0.4	0.5	1.9	ND	2100	13	57	NA	3.2	NA
102	SA2	14.21	ND	0.03	ND	ND	ND	1.7	ND	0.1	0.2	NA	NA	NA	NA	NA	NA	2.9	NA
107	SA2	15.29	ND	0.04	ND	ND	ND	0.4	ND	ND	0	1.9	ND	1800	15	48	NA	3	NA
106	SA2	15.79	ND	0.05	ND	ND	ND	0.7	ND	ND	0.1	NA	NA	NA	NA	NA	0.3	3	NA
105	SA2	16.29	ND	0.05	ND	ND	ND	0.8	ND	ND	0	NA	NA	NA	NA	NA	NA	3.1	NA
104	SA2	16.79	ND	0.03	ND	ND	ND	1.2	ND	ND	0.1	1.9	ND	1700	0.8	11	NA	3.1	NA
109	SA2	18.79	ND	0.03	ND	ND	ND	1	ND	ND	0.1	1.9	4.5	1300	2	83	0.2	3	NA
108	SA2	19.29	ND	0.02	ND	ND	ND	0.7	ND	ND	0.1	2.7	5.5	1200	10	37	NA	3.1	NA
171	DG1A	7.29	ND	0.09	ND	ND	ND	1.6	ND	ND	0.2	NA	NA	NA	NA	NA	NA	2.6	NA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
170	DG1A	7.79	ND	0.02	ND	ND	ND	6	ND	ND	0.6	1.9	ND	480	17	2600	NA	2.6	NA
169	DG1A	8.29	ND	0.01	ND	ND	0.2	0.3	ND	0.6	1.7	NA	NA	NA	NA	NA	NA	2.8	NA
168	DG1A	8.79	ND	0.14	0.13	ND	1.4	1.3	ND	1.1	0.8	62	34	680	6.7	1100	0.4	3	NA
167	DG1A	9.29	ND	0.3	1.8	ND	7.5	1.5	ND	4.4	0.9	2.1	1.9	780	0.4	3400	NA	2.8	NA
175	DG1A	10.71	ND	0.01	ND	ND	ND	7.7	ND	5.9	8	NA	NA	NA	NA	NA	NA	2.7	NA
174	DG1A	10.79	ND	ND	ND	ND	ND	2.8	ND	2.4	3.3	19	8.5	910	10	1300	6	2.7	NA
173	DG1A	11.29	ND	ND	ND	ND	ND	11	ND	5.1	11	1.9	1.5	1300	12	1700	NA	2.4	ND
172	DG1A	11.79	ND	0.01	ND	ND	ND	11	ND	2.2	11	NA	NA	NA	NA	NA	NA	2.7	NA
181	DG1A	12.21	ND	ND	ND	ND	0.2	2.1	ND	0.1	2.7	NA	NA	NA	NA	NA	NA	2.7	NA
180	DG1A	12.29	ND	ND	ND	ND	0.3	2.1	ND	0.1	2.4	13	12	860	11	1600	NA	2.9	NA
179	DG1A	12.79	ND	ND	ND	ND	0.3	2.8	ND	0.1	2.8	3.9	1.8	800	14	3200	NA	2.9	NA
178	DG1A	13.29	ND	ND	ND	ND	ND	1.9	ND	ND	1.2	NA	NA	NA	NA	NA	NA	3.2	NA
177	DG1A	13.79	ND	ND	ND	ND	ND	1.5	ND	ND	0.9	7.5	37	430	7.7	69	NA	3.2	NA
176	DG1A	14.29	ND	0	ND	ND	ND	1.1	ND	ND	0.5	NA	NA	NA	NA	NA	NA	3.1	NA
186	DG1A	14.79	ND	ND	ND	ND	ND	0.8	ND	ND	0.3	11	54	630	9.7	32	NA	3	NA
185	DG1A	15.29	ND	ND	ND	ND	ND	0.5	ND	ND	0.2	2.7	42	570	11	60	0.3	3.1	NA
184	DG1A	15.79	ND	0.01	ND	ND	ND	0.4	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	ND
183	DG1A	16.29	ND	0	ND	ND	ND	0.2	ND	ND	0.1	2.2	22	530	9.5	320	NA	3.1	NA
182	DG1A	16.79	ND	ND	ND	ND	ND	0.4	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	NA
191	DG1A	17.29	ND	ND	ND	ND	ND	0.3	ND	ND	0	17	28	700	16	660	0.6	3.1	NA
190	DG1A	17.79	ND	ND	ND	ND	ND	0.1	ND	ND	0	NA	NA	NA	NA	NA	NA	2.9	NA
189	DG1A	18.29	ND	ND	ND	ND	ND	0.1	ND	ND	0	1.9	20	570	6.7	230	NA	3.1	ND
188	DG1A	18.79	ND	ND	ND	ND	ND	0.1	ND	ND	0	NA	NA	NA	NA	NA	NA	3.1	NA
187	DG1A	19.29	ND	ND	ND	ND	ND	0.1	ND	ND	0	1.9	81	17	ND	19	NA	3.2	NA
196	DG1B	7.29	ND	ND	ND	ND	0.1	7.8	ND	0.1	0.3	1.9	ND	410	13	1800	NA	2.6	NA
195	DG1B	7.79	ND	ND	ND	ND	ND	4.1	ND	0	0.1	NA	NA	NA	NA	NA	NA	2.5	NA
194	DG1B	8.29	ND	ND	ND	ND	ND	17	ND	ND	1.2	1.9	ND	340	17	1700	1.9	2.9	NA
193	DG1B	8.54	ND	ND	ND	ND	ND	7.1	ND	ND	1.2	NA	NA	NA	NA	NA	NA	2.6	NA
192	DG1B	9.29	ND	0.04	ND	ND	ND	2.9	ND	1	2.1	1.9	ND	440	11	660	NA	3	NA
200	DG1B	10.29	ND	ND	0.12	ND	0.8	5.5	ND	3.4	4.2	1.9	ND	870	17	3200	NA	2.5	NA
199	DG1B	10.79	ND	ND	0.25	ND	1.4	4.4	ND	3.1	3.7	NA	NA	NA	NA	NA	NA	2.4	NA
198	DG1B	11.29	ND	ND	ND	ND	0.7	12	ND	6.5	7.8	2	2.2	33	ND	53	NA	2.4	ND
197	DG1B	11.79	ND	ND	ND	ND	1.2	5.3	ND	4	4.1	1.9	ND	740	0.9	2900	NA	2.5	NA
205	DG1B	12.71	ND	ND	ND	ND	ND	6.9	ND	0.3	1	NA	NA	NA	NA	NA	NA	2.6	NA
204	DG1B	12.79	ND	ND	ND	ND	ND	11	ND	0.3	1.4	1.9	ND	1000	12	5400	3.3	2.5	NA
203	DG1B	13.29	ND	ND	ND	ND	ND	9.2	ND	0	0.9	1.9	ND	650	11	2900	NA	2.8	NA
202	DG1B	13.79	ND	ND	ND	ND	ND	10	ND	ND	1	NA	NA	NA	NA	NA	NA	2.4	NA
201	DG1B	14.29	ND	ND	ND	ND	ND	16	ND	ND	1.2	1.9	ND	27	ND	110	NA	2.7	NA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
210	DG1B	14.79	ND	ND	ND	ND	ND	4.4	ND	ND	0.4	25	9.6	20	ND	98	NA	2.9	NA
209	DG1B	15.29	ND	ND	ND	ND	ND	2.5	ND	ND	0.2	NA	NA	NA	NA	NA	NA	2.8	NA
208	DG1B	15.79	ND	ND	ND	ND	ND	1	ND	ND	0	14	52	14	ND	15	0.2	3.2	NA
207	DG1B	16.29	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA	3.2	NA
206	DG1B	16.79	ND	ND	ND	ND	ND	0.9	ND	ND	0	2.5	9.6	17	ND	9	NA	3.1	NA
215	DG1B	17.29	ND	ND	ND	ND	ND	0.3	ND	ND	0	NA	NA	NA	NA	NA	NA	3.2	NA
214	DG1B	17.79	ND	ND	ND	ND	ND	0.3	ND	ND	ND	24	NA	1.4	ND	ND	0.1	3.2	NA
213	DG1B	18.29	ND	ND	ND	ND	ND	0.2	ND	ND	0	NA	NA	NA	NA	NA	NA	3	NA
212	DG1B	18.79	ND	ND	ND	ND	ND	0.1	ND	ND	ND	4.7	31	15	ND	10	NA	2.9	NA
211	DG1B	19.29	ND	ND	ND	ND	ND	0.1	ND	ND	ND	NA	NA	NA	NA	NA	NA	3.2	NA
137	DG2A	3.29	ND	0.02	0.05	ND	ND	1.5	ND	ND	0	NA	NA	NA	NA	NA	NA	3.2	NA
136	DG2A	3.79	ND	0.03	0.85	0	0.5	0.9	ND	ND	0	1.5	11	130	8.4	14	0.6	3.3	NA
135	DG2A	4.29	ND	0.1	ND	ND	ND	0.6	ND	ND	0	1.9	10	220	0.7	98	NA	3	NA
139	DG2A	6.29	ND	ND	ND	ND	ND	0.6	ND	ND	0	1.9	4.4	240	6.9	230	NA	3	NA
138	DG2A	6.79	ND	ND	ND	ND	ND	1.1	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	NA
143	DG2A	8.21	ND	1.5	1.9	0	0.5	0.6	ND	0	0	NA	NA	NA	NA	NA	NA	2.8	NA
142	DG2A	8.29	ND	21	22	0.2	7.5	0.5	ND	0	0	1.9	ND	250	13	2100	NA	2.9	NA
141	DG2A	8.79	ND	300	77	0.4	5.3	0.5	ND	0.2	0.1	160	56	880	19	4300	NA	2.7	NA
140	DG2A	9.29	ND	670	43	0.2	2.1	0.8	0	0.2	0.1	560	180	1600	13	6700	26	2.3	NA
148	DG2A	9.79	ND	130	0.59	ND	ND	0.1	0	0	0	8.6	ND	600	15	810	NA	3.2	NA
147	DG2A	10.29	ND	76	0.71	ND	ND	0.1	ND	ND	ND	NA	NA	NA	NA	NA	NA	3.1	NA
146	DG2A	10.79	ND	190	0.98	ND	ND	0.1	ND	ND	0	1.9	1.5	560	13	260	NA	2.7	NA
145	DG2A	11.29	0	290	3.5	0	0.2	0.1	0	0	0	NA	NA	NA	NA	NA	NA	2.7	NA
144	DG2A	11.79	ND	7300	170	ND	ND	0.2	ND	ND	ND	45	9.3	980	18	5000	NA	2.7	NA
152	DG2A	12.79	ND	160	1.7	ND	ND	0.1	0	0	0	NA	NA	NA	NA	NA	NA	3.1	NA
151	DG2A	13.29	0.1	260	1.2	0	ND	0	ND	ND	0	2.5	24	550	7.7	180	NA	3.1	NA
150	DG2A	13.79	ND	90	1.1	0	ND	0.1	0	0	0	NA	NA	NA	NA	NA	NA	3.1	NA
149	DG2A	14.29	ND	120	0.89	0	0.1	0.1	0	0	0	13	24	720	17	240	NA	3.1	NA
161	DG2A	14.79	ND	97	1.3	ND	ND	0.2	0	0	0.2	3	12	840	16	400	0.2	2.9	NA
160	DG2A	15.29	ND	82	1.4	0	0.1	0.2	0	0	0.2	NA	NA	NA	NA	NA	NA	3	NA
159	DG2A	15.79	ND	66	1.4	ND	ND	0.2	0	0.1	0.3	1.5	5.8	710	8.9	440	NA	3	NA
158	DG2A	15.88	ND	120	2.4	ND	ND	0.1	0	0	0.2	NA	NA	NA	NA	NA	NA	3	NA
157	DG2A	15.96	ND	97	2	0	ND	0.1	0	ND	0.2	NA	NA	NA	NA	NA	NA	3	NA
156	DG2A	16.04	ND	93	1.8	ND	ND	0.2	0	0.1	0.4	NA	NA	NA	NA	NA	NA	3.1	NA
155	DG2A	16.13	ND	160	2.6	ND	ND	0.1	0	0	0.2	NA	NA	NA	NA	NA	NA	3.1	NA
154	DG2A	16.29	ND	100	1.9	ND	ND	0.2	0	0.1	0.3	1.9	6.7	650	8.3	410	NA	3	NA
153	DG2A	16.79	ND	61	1.9	ND	ND	0.1	0	0	0.2	NA	NA	NA	NA	NA	NA	3	NA
166	DG2A	17.29	ND	120	2.4	ND	ND	0.2	0	0	0.2	1.9	1.5	32	ND	43	NA	2.8	NA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
165	DG2A	17.79	ND	130	2.3	ND	ND	0.2	0	0.1	0.3	NA	NA	NA	NA	NA	NA	2.9	NA
164	DG2A	18.29	ND	120	2.4	ND	ND	0.1	0	0	0.1	2.5	3	720	10	390	NA	3	NA
163	DG2A	18.79	ND	140	1.2	ND	ND	0.1	0	ND	0.1	NA	NA	NA	NA	NA	NA	2.9	NA
162	DG2A	19.29	ND	180	0.73	ND	ND	0.1	0	0	0	1.9	ND	750	8.6	530	0.2	2.8	NA
111	DG2B	3.71	ND	0.03	ND	ND	ND	2	ND	ND	0	NA	NA	NA	NA	NA	NA	3	NA
110	DG2B	4.29	ND	0.02	ND	ND	ND	4.1	ND	ND	0	2.4	ND	52	1	1200	NA	3.2	NA
115	DG2B	5.71	ND	0	ND	ND	ND	2.9	ND	ND	0	1.9	21	130	2.6	170	NA	2.9	NA
114	DG2B	5.79	ND	ND	ND	ND	ND	3.3	ND	ND	0.1	NA	NA	NA	NA	NA	NA	2.8	NA
113	DG2B	6.29	ND	ND	0.02	ND	ND	3.6	ND	0	0.9	NA	NA	NA	NA	NA	NA	2.8	NA
112	DG2B	6.79	ND	ND	1.9	ND	1.7	2.9	ND	0.6	0.6	7.3	3.7	88	0.6	2900	1.1	2.8	NA
117	DG2B	8.79	0	0.01	0.8	0	0.9	2.6	ND	0.4	0.4	40	17	110	9.8	1700	1.2	2.8	NA
116	DG2B	9.29	ND	ND	5.2	ND	11	4.4	ND	1.6	0.8	110	38	170	11	3300	NA	2.6	NA
120	DG2B	10.79	ND	ND	0.87	1.5	2	3.8	ND	3.1	1	69	17	9.4	ND	87	NA	3	NA
119	DG2B	11.29	ND	ND	1.7	ND	3.1	1.6	ND	1.7	0.5	NA	NA	NA	NA	NA	NA	3.1	NA
118	DG2B	11.79	ND	ND	5.2	ND	1.4	2.8	ND	3.1	0.6	2.1	14	290	9.6	26	NA	3	NA
124	DG2B	13.21	ND	1.1	8.7	0	5.6	0.5	ND	0.7	0.2	NA	NA	NA	NA	NA	NA	3	NA
123	DG2B	13.29	ND	0.61	5.7	ND	4.2	1.1	ND	1	0.2	1.9	3.3	330	11	170	1.7	3.1	NA
122	DG2B	13.79	ND	3.8	7.9	ND	4.7	0.9	ND	1	0.2	NA	NA	NA	NA	NA	NA	3.1	NA
121	DG2B	14.29	ND	11	6.1	ND	2.9	1.3	ND	1.7	0.2	4.3	37	390	8.2	37	NA	3.1	NA
129	DG2B	14.79	ND	35	8.3	ND	2.8	0.5	ND	0.4	0	2.7	11	550	20	320	NA	3.1	NA
128	DG2B	15.29	ND	45	6.5	0	1.3	0.4	ND	0.5	0	NA	NA	NA	NA	NA	NA	3.1	NA
127	DG2B	15.79	ND	75	7.9	ND	1.5	0.4	ND	0.5	0	1.2	8.1	460	11	170	NA	3.1	NA
126	DG2B	16.29	ND	31	3.9	ND	0.3	0.3	ND	0.3	0	NA	NA	NA	NA	NA	NA	3.2	NA
125	DG2B	16.79	ND	31	3.4	ND	ND	0.1	ND	0.1	0	1.9	5.3	480	11	320	NA	3.1	NA
134	DG2B	17.29	ND	42	2.8	ND	0.6	0.2	ND	0.1	0	NA	NA	NA	NA	NA	NA	3.2	NA
133	DG2B	17.79	ND	28	1.8	ND	0.1	0.1	ND	0	ND	2.8	13	17	ND	26	0.2	3.2	NA
132	DG2B	18.29	ND	28	2	ND	0.2	0.1	ND	0	ND	NA	NA	NA	NA	NA	NA	3.2	NA
131	DG2B	18.79	ND	32	1.8	ND	0.1	0.1	ND	0	ND	7.3	84	470	10	160	NA	3.1	NA
130	DG2B	19.29	ND	27	1.4	ND	ND	0.1	ND	0	ND	NA	NA	NA	NA	NA	NA	3	NA

APPENDIX A POINTS OF CONTACT

Point of Contact Name	Organization Name Address	Phone Email	Role in Project
Dr. Mitchell Olson	Trihydro Corporation 1537 Riverside Ave Fort Collins, CO 80524	P: (970) 492-6022 E: molson@trihydro.com	Co-Principal Investigator
Dr. Wilson Clayton	W.S. Clayton, Ltd. 28599 Buchanan Dr., Evergreen, CO 80439, as contractor to Trihydro Corp.	P: (303) 679-3143 E: wilson@wsclayton.com	Principal Investigator
Dr. Tom Sale	Colorado State University 1320 Campus Delivery Fort Collins, CO 80523	P: (970) 491-8413 E: tsale@engr.colostate.edu	Tech support and oversight of laboratory processing and analysis
Dr. Susan DeLong	Colorado State University 1320 Campus Delivery Fort Collins, CO 80523	P: (970) 491-6606 E: susan.de_long@colostate.edu	Microbiological analysis support
Maria Irianni-Renno	Colorado State University 1320 Campus Delivery Fort Collins, CO 80523	P: (970) 491-8647 E: mmiriann@eagle.fgcu.edu	Field and laboratory support
Dr. Rick Johnson	Oregon Health & Science University Gaines Hall, Room 233 3181 SW Sam Jackson Park Rd Portland, OR 97239	P: (503) 346-3432 E: rick.johnson.phd@gmail.com	Tech support
Rick Rogers	Drilling Engineers, Inc. 1309 Duff Dr Fort Collins, CO 80522	P: (970) 484-5183 E: rick@drillingengineers.com	Drilling contractor

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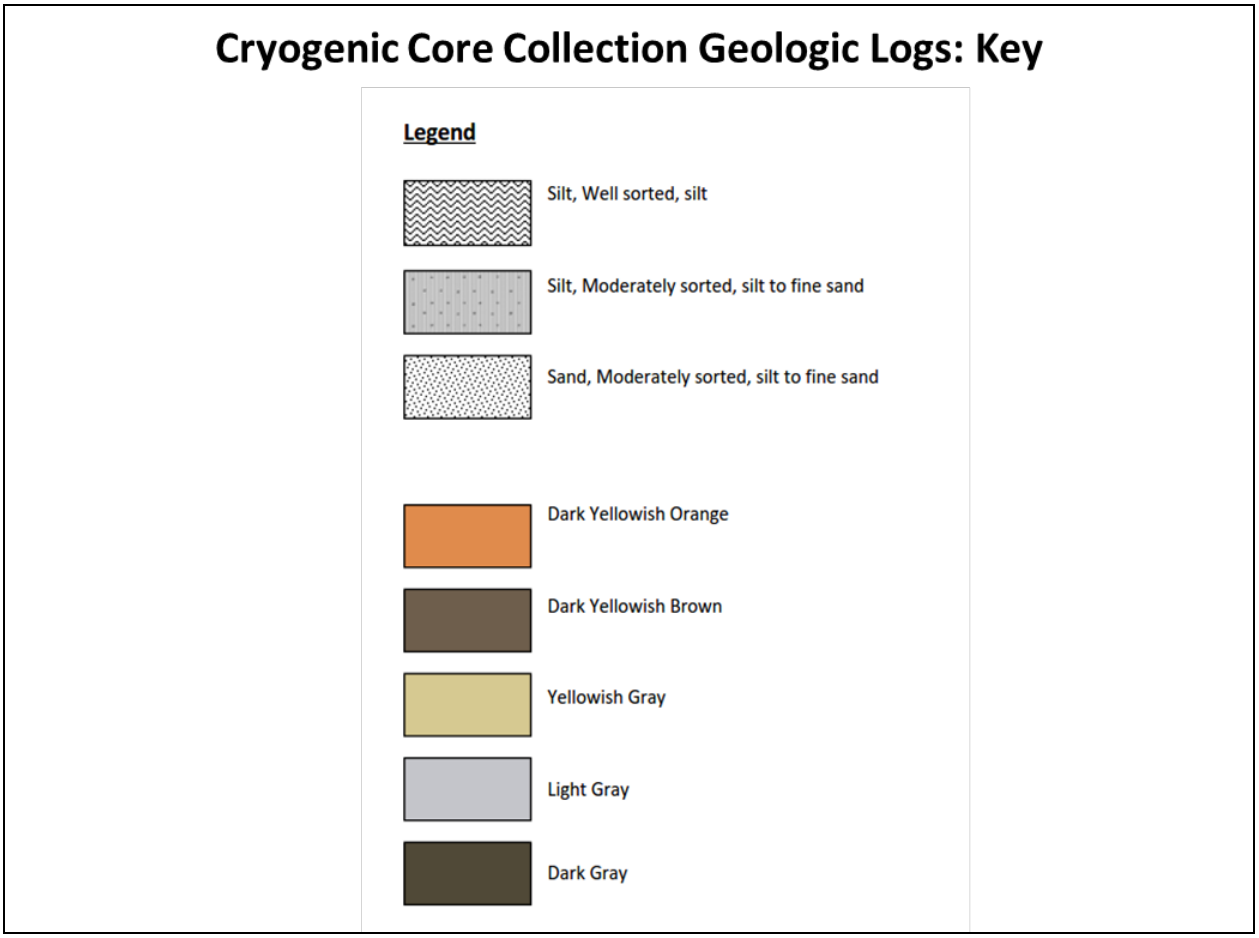
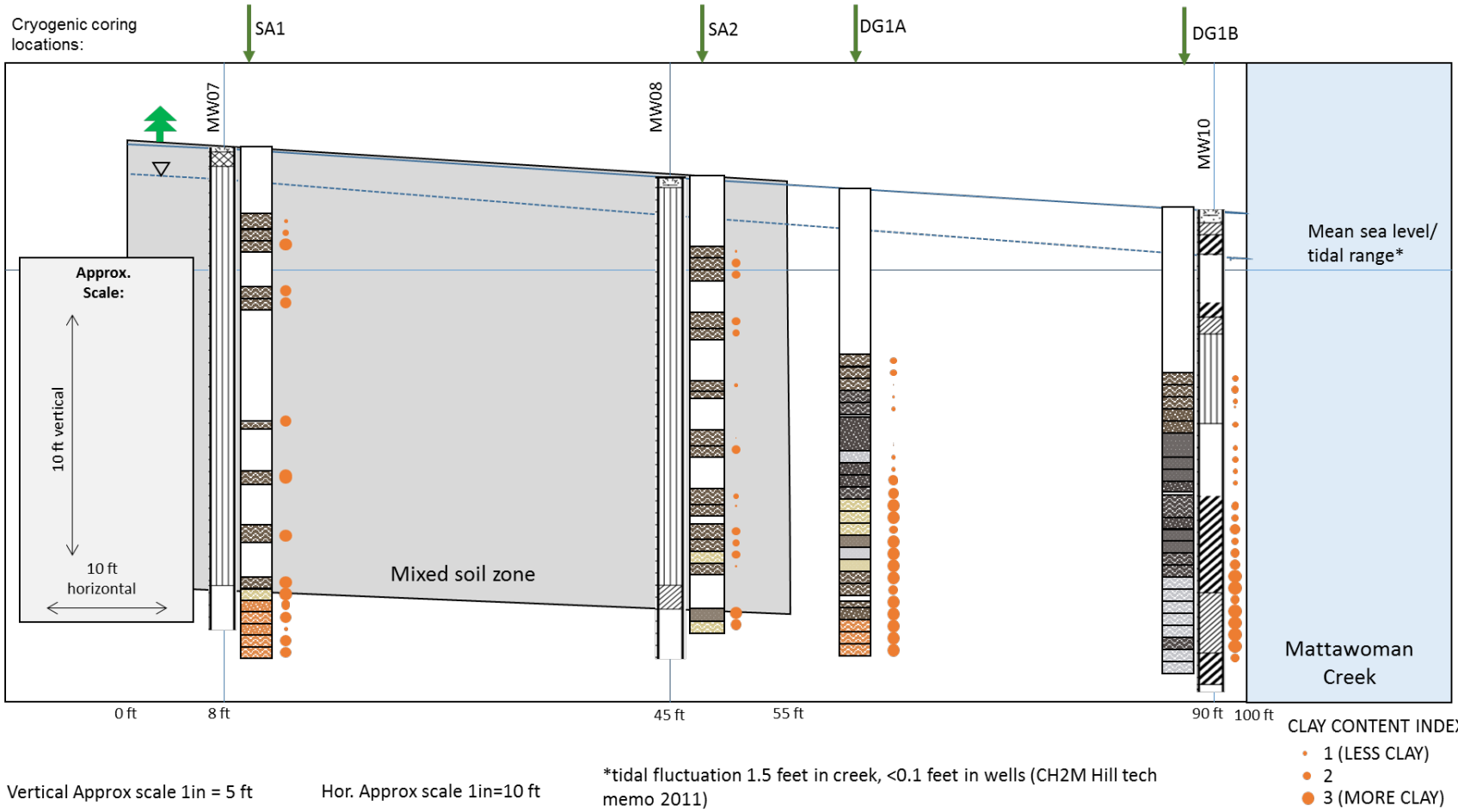
APPENDIX B GEOLOGIC LOGS

Geologic cross-section plots are shown in landscape orientation on the following pages.



Geology Data Cross Section: Transect DG1

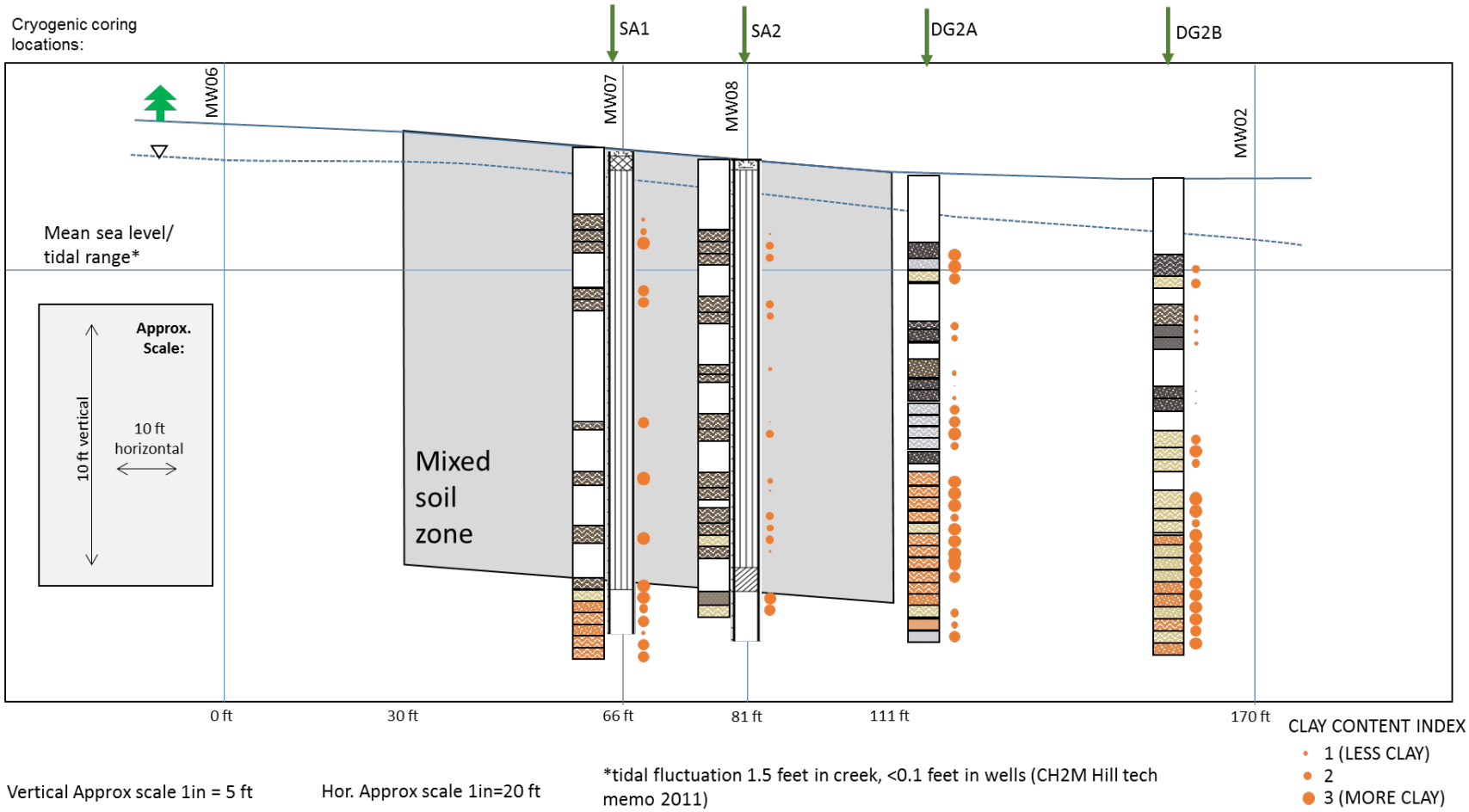


Vertical Approx scale 1in = 5 ft

Hor. Approx scale 1in=10 ft

*tidal fluctuation 1.5 feet in creek, <0.1 feet in wells (CH2M Hill tech memo 2011)

Geology Data Cross Section: Transect DG2



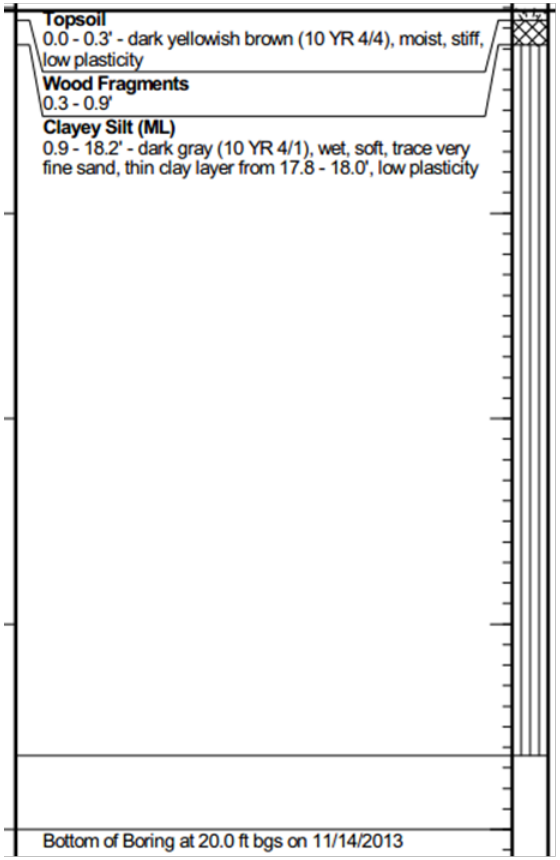
Vertical Approx scale 1in = 5 ft

Hor. Approx scale 1in=20 ft

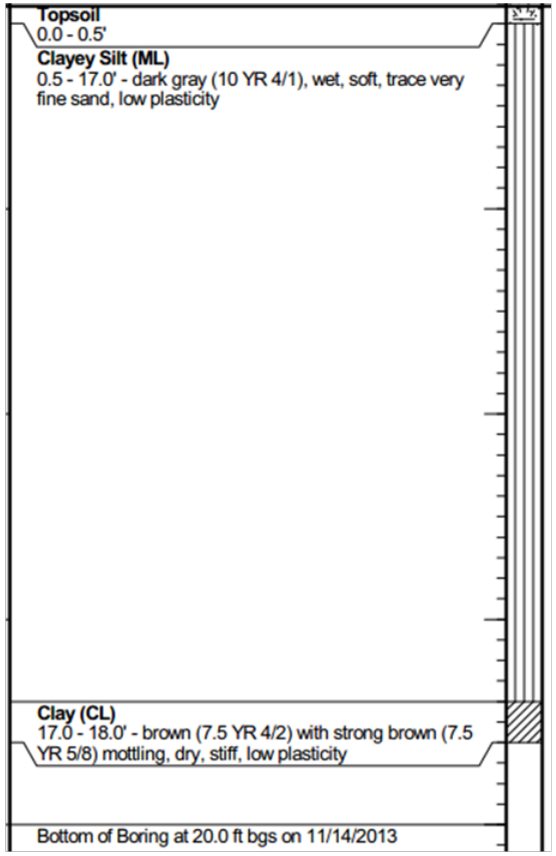
*tidal fluctuation 1.5 feet in creek, <0.1 feet in wells (CH2M Hill tech memo 2011)

Existing Geologic Logs: Details

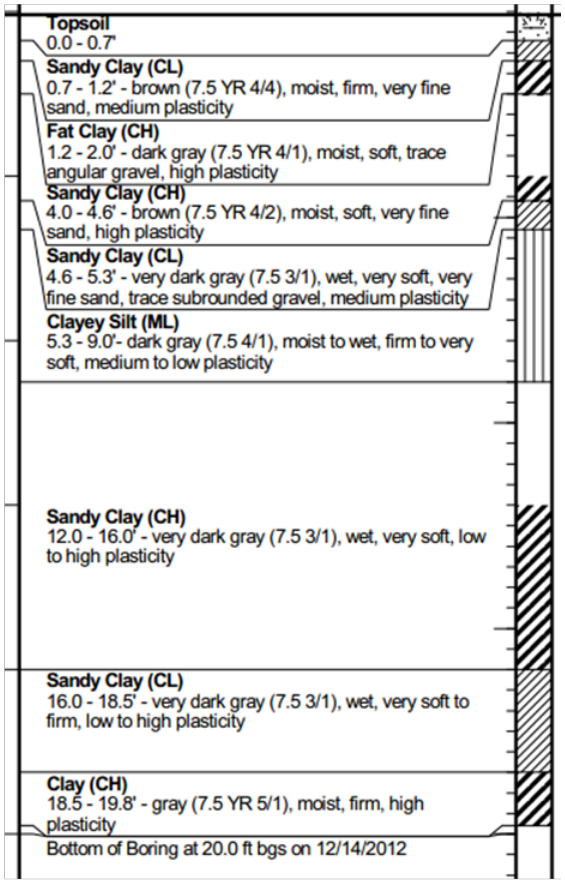
MW07*



MW08*

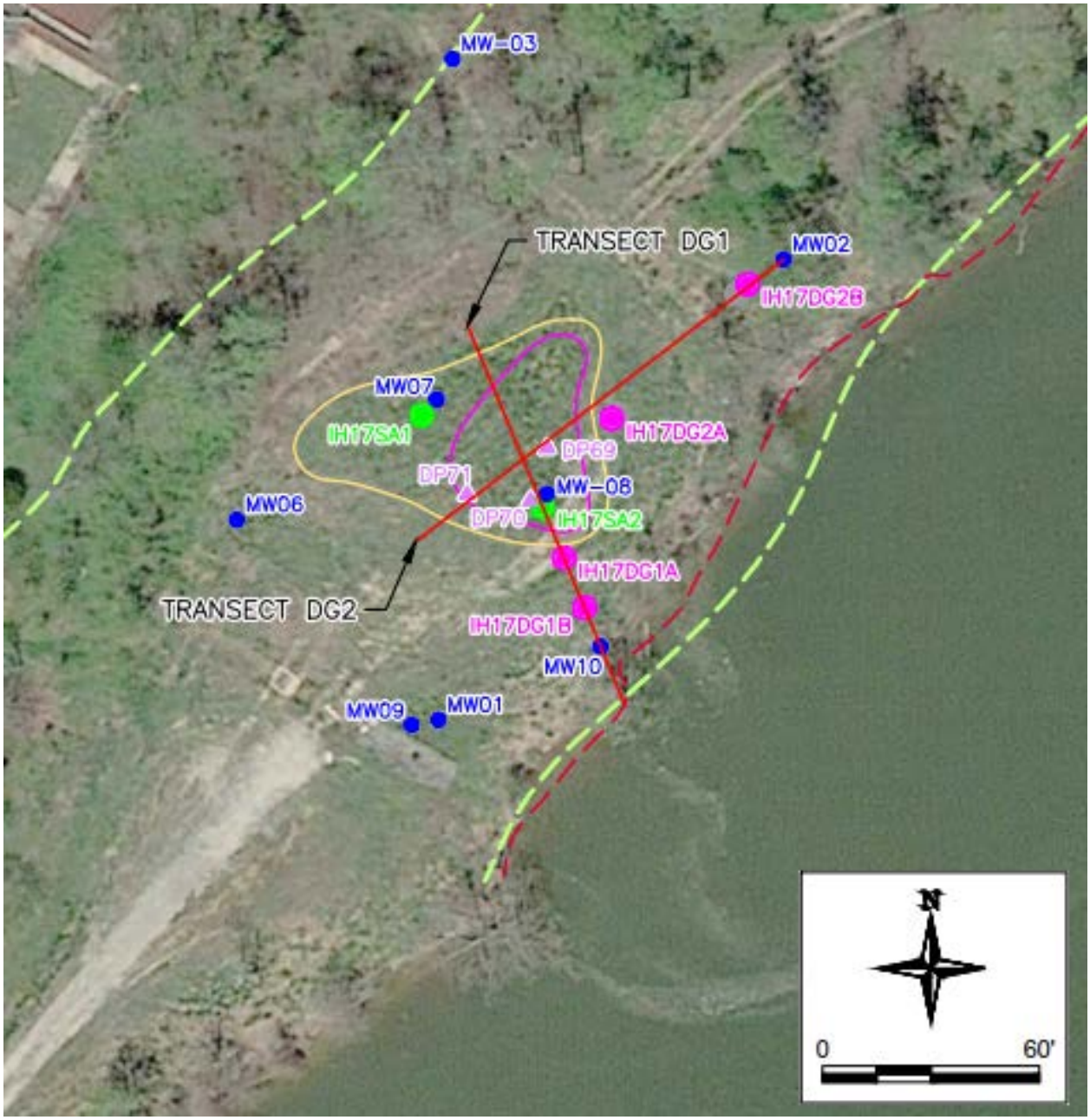


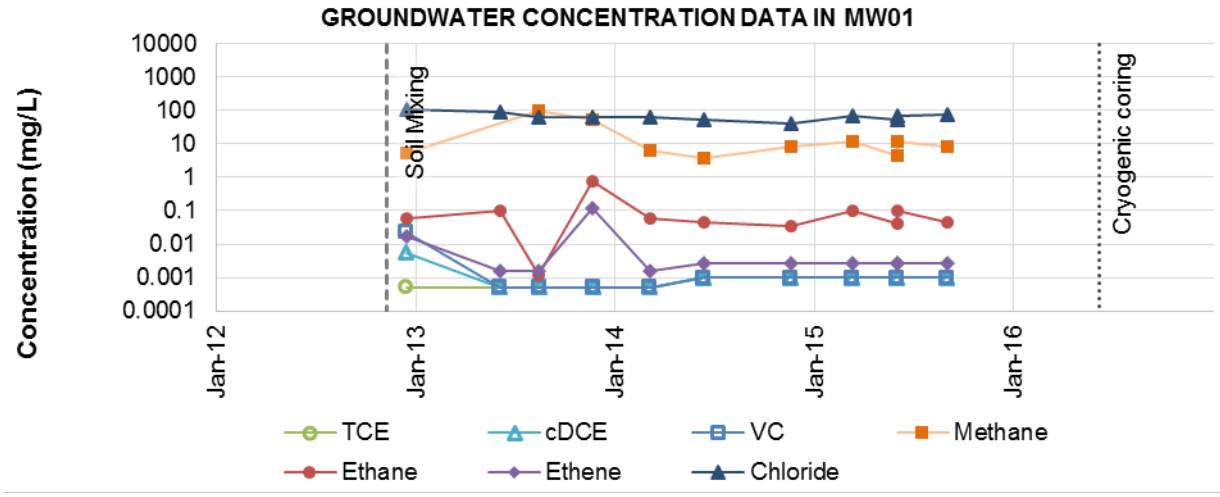
MW10*

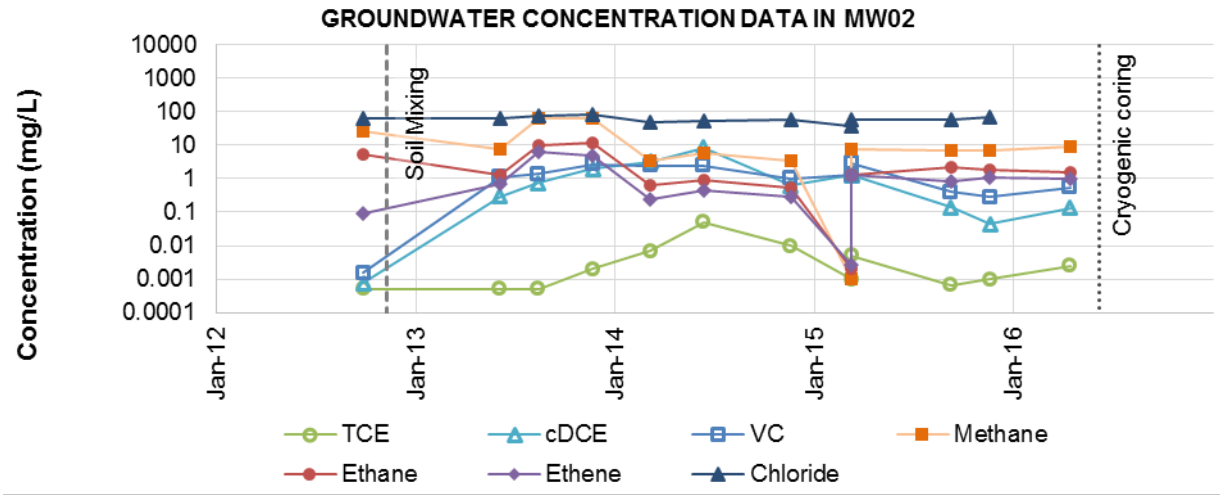


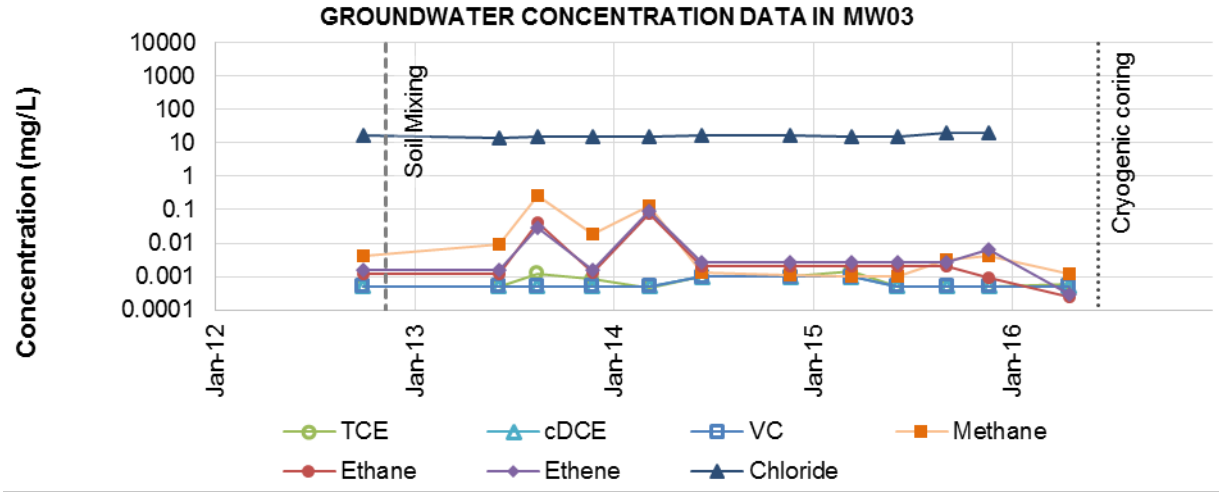
*CH2M HILL 2014

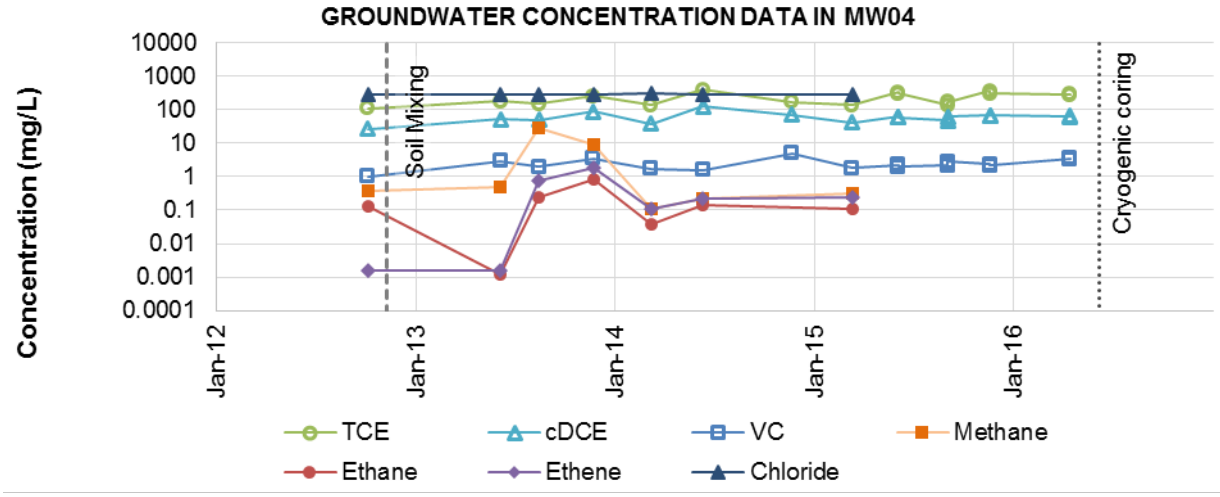
APPENDIX C PREVIOUSLY EXISTING GROUNDWATER DATA

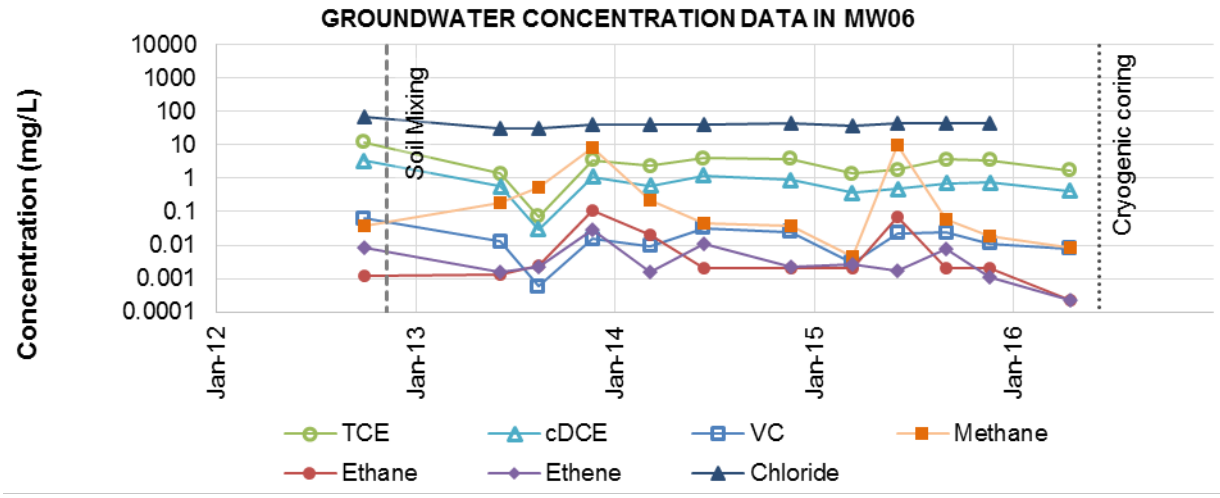


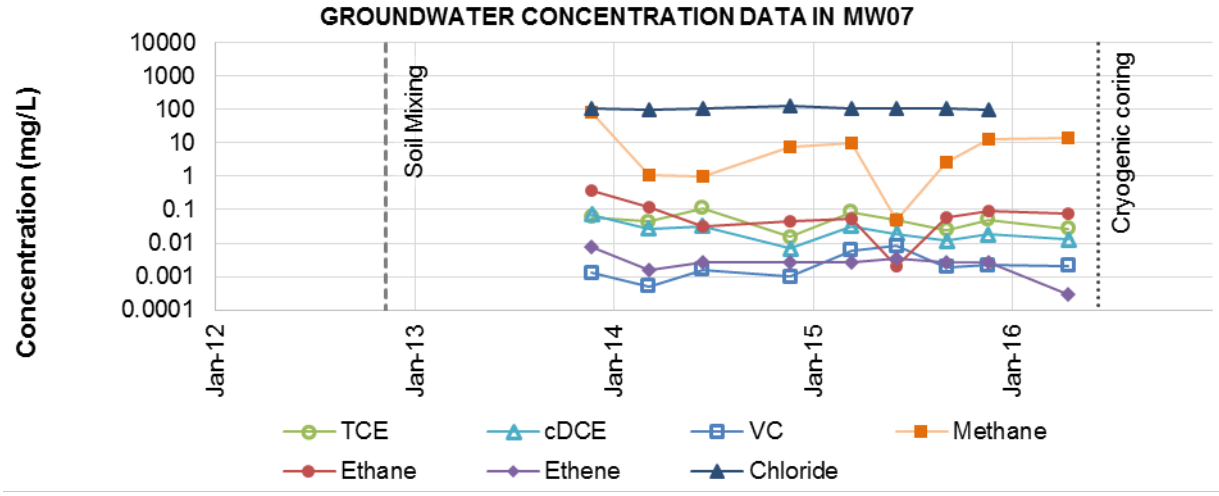

GROUNDWATER CONCENTRATION DATA IN MW01
Concentration (mg/L)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride

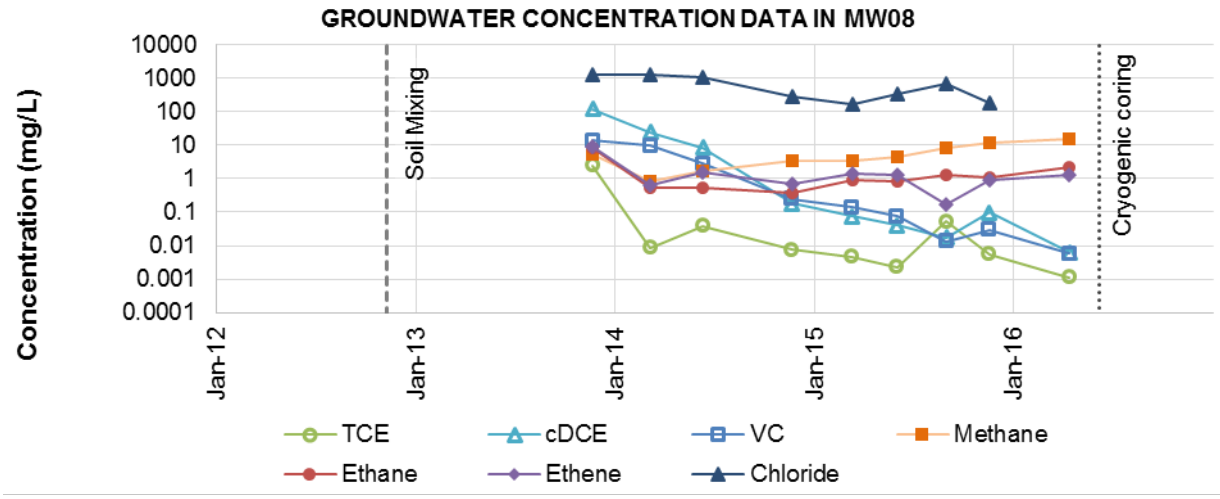

GROUNDWATER CONCENTRATION DATA IN MW02
Concentration (mg/L)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW03
Concentration (mg/L)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW04
Concentration (mg/L)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW06
Concentration (mg/L)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW07
Concentration (mg/L)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride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10
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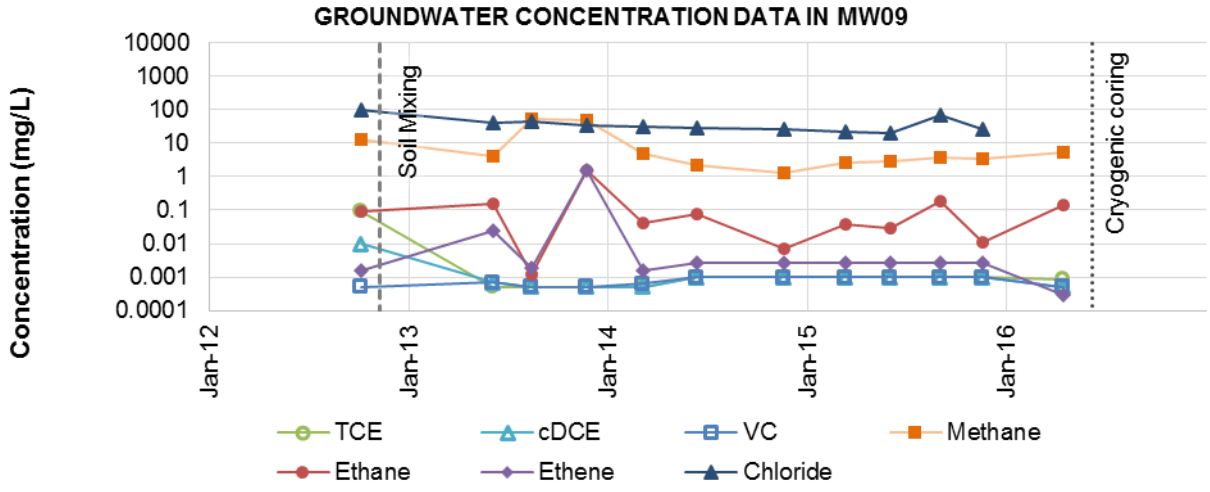
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride


GROUNDWATER CONCENTRATION DATA IN MW09
Concentration (mg/L)
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100
10
1
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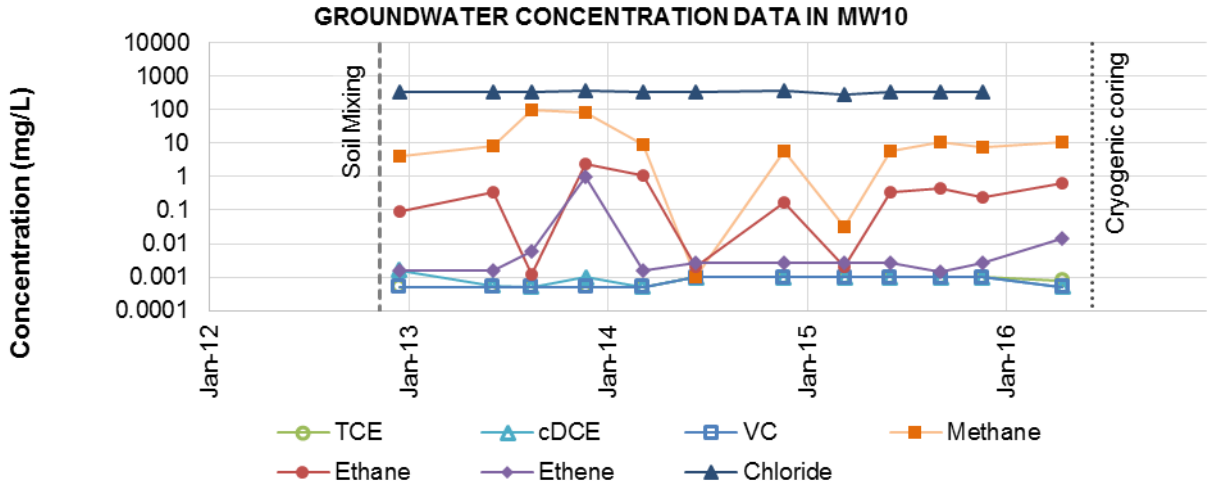
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride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100
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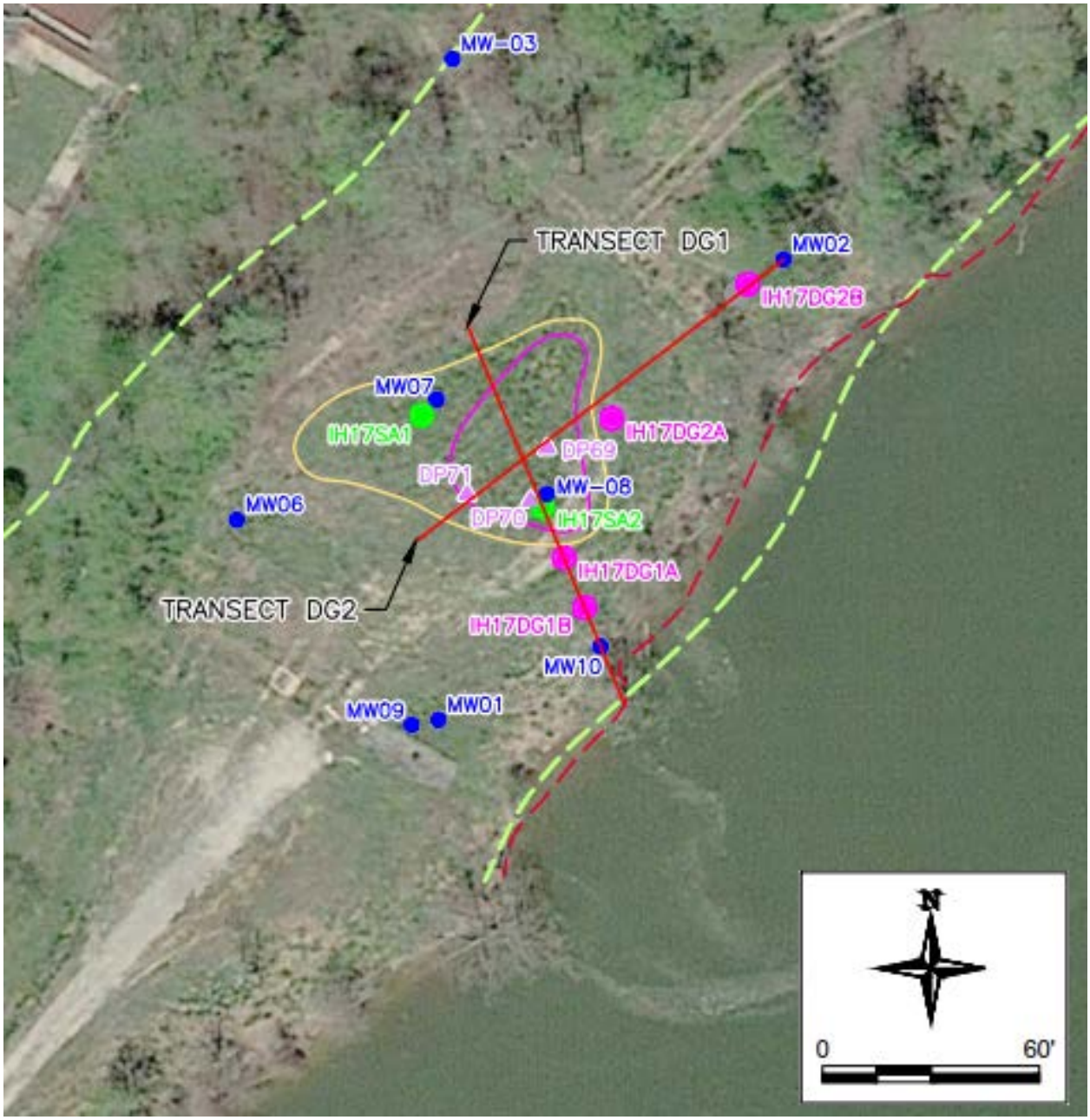
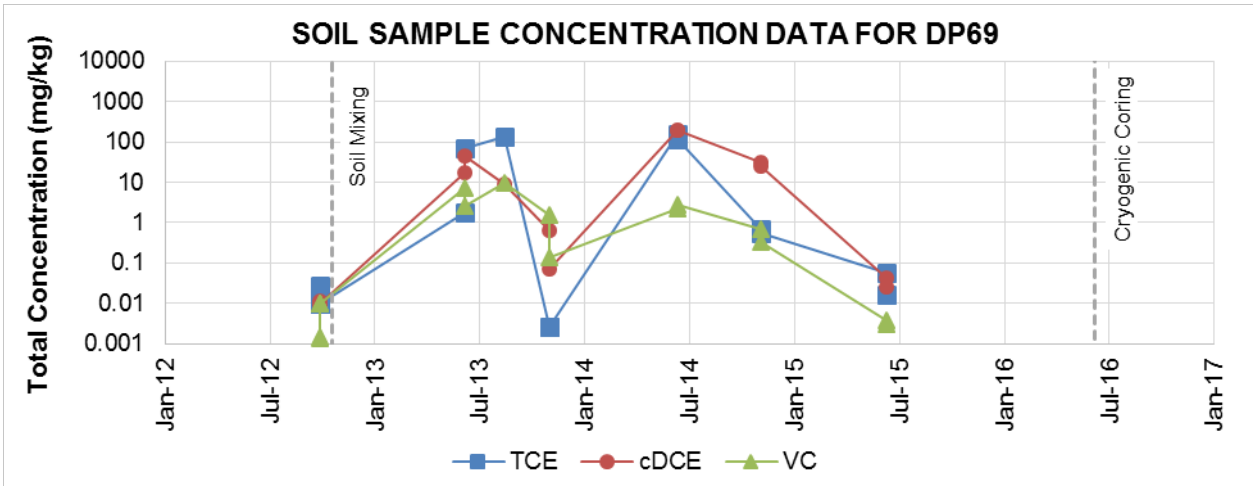
0.1
0.01
0.001
0.0001
Soil Mixing
Cryogenic coring
Jan-12
Jan-13
Jan-14
Jan-15
Jan-16
TCE
cDCE
VC
Methane
Ethane
Ethene
Chloride

APPENDIX D PREVIOUSLY EXISTING SOIL DATA




SOIL SAMPLE CONCENTRATION DATA FOR DP69
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10
1
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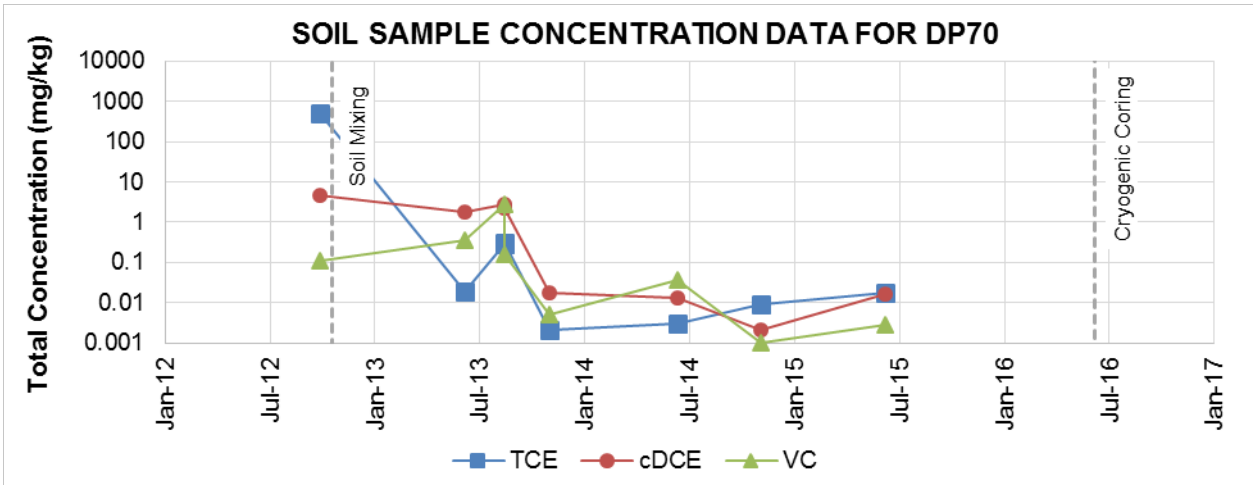
0.01
0.001
Soil Mixing
Cryogenic Coring
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
TCE
cDCE
VC


SOIL SAMPLE CONCENTRATION DATA FOR DP70
Total Concentration (mg/kg)
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100
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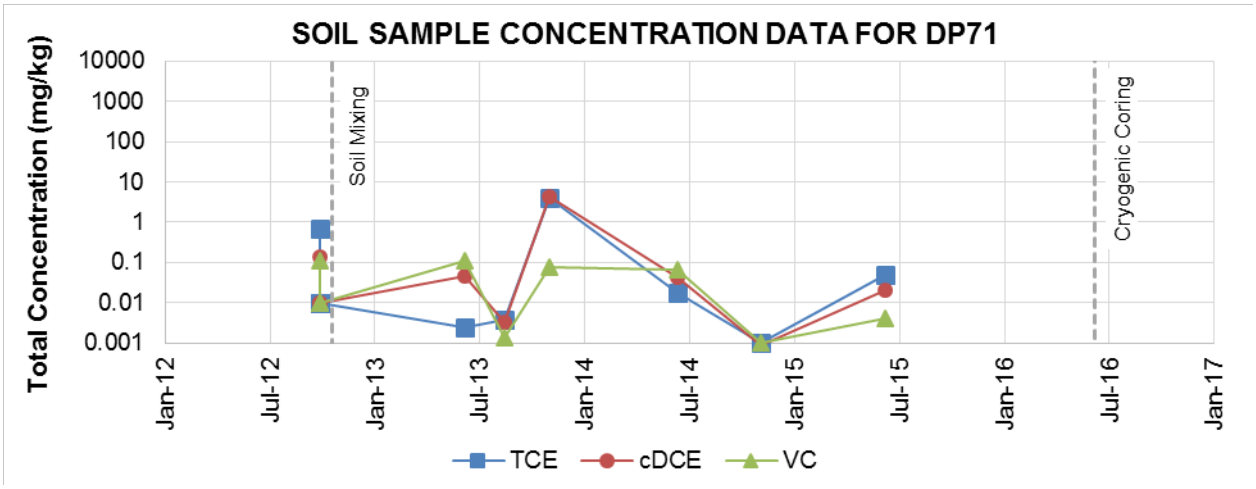
0.1
0.01
0.001
Soil Mixing
Cryogenic Coring
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
TCE
cDCE
VC


SOIL SAMPLE CONCENTRATION DATA FOR DP71
Total Concentration (mg/kg)
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1000
100
10
1
0.1
0.01
0.001
Soil Mixing
Cryogenic Coring
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
TCE
cDCE
VC

APPENDIX E PHOTOGRAPHIC LOG


NITROGEN
NITROGEN
PENSKE


CENTRAL MINE
EQUIPMENT CO.


TRAL MINE
EQUIPMENT CO.


HONDA

APPENDIX F QUALITY ASSURANCE

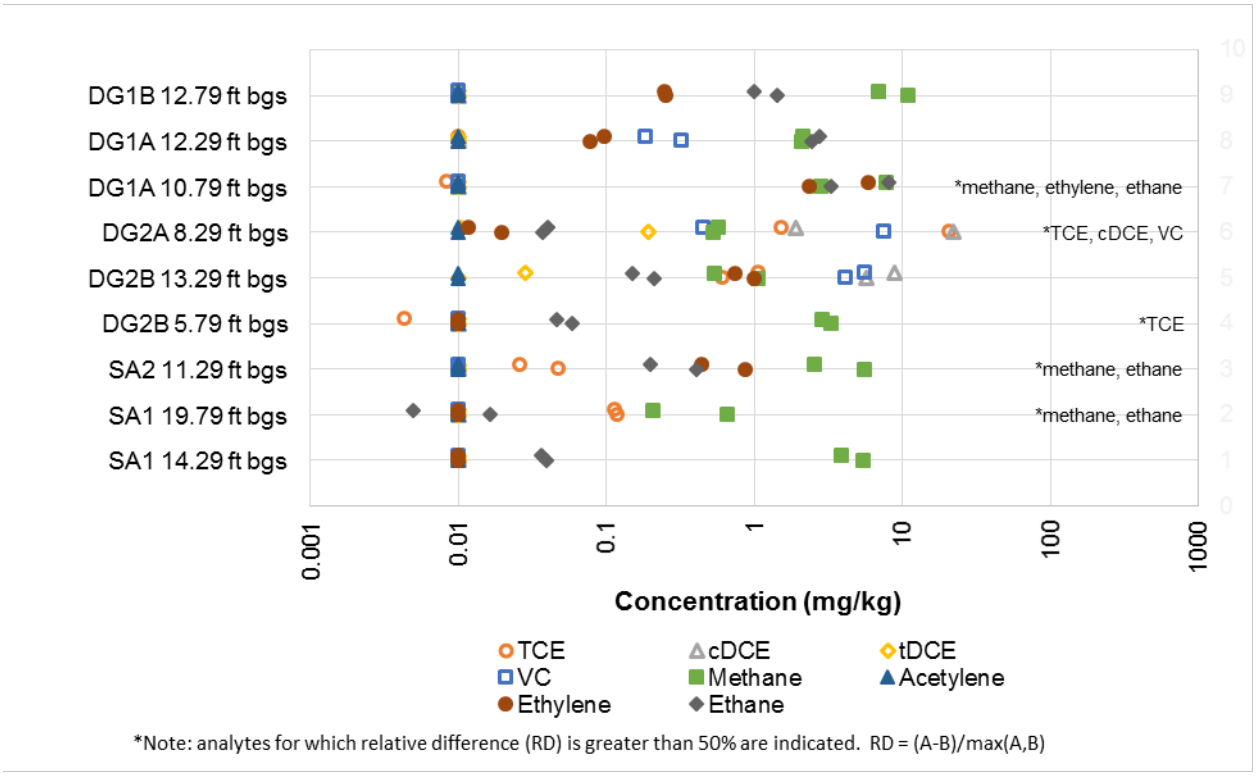
Calibration

With a few exceptions, the analyses were conducted in the laboratory at CSU. Analytical instruments and analyses are described in Section 5.6.2. Calibration standards were prepared and analyzed to generate response factors. Calibration curves were generated using at least five concentrations, bracketing the range of concentrations expected for the field samples.

Quality Assurance Sampling

For frozen soil cores, standard quality assurance (QA) samples such as equipment blanks, trip blanks, and field blanks are not applicable. Duplicate subsamples were collected in the laboratory at a rate of one duplicate per 20 depth-discrete subsamples. Duplicate samples were collected from depths adjacent to the depth of the normal sample. Laboratory blanks were prepared to correspond with each type of laboratory extraction procedure (i.e., methanol- and water-based extraction). In addition, one sample from each core was sent to an external lab for confirmatory analysis.

Results of duplicate sample analyses are presented in the following chart. The duplicate samples are imperfect in that samples represent different sample depths, but the depths are adjacent. For each duplicate sample, analytes for which the relative difference (RD) is greater than 50% are indicated.



Decontamination Procedures

Drilling equipment was decontaminated between each location and before demobilization from the site. Decontamination consisted of steam/pressure washing to remove potentially contaminated soils adhering to drilling equipment and water rinsing. Before the field personnel demobilized from Site 17, Indian Head site personnel provided approval that cleanup procedures were adequate.

Decontamination in the laboratory was conducted in accordance with the high throughput analysis protocol (Sale et al. 2016). Cross-contamination risk is greatly reduced when working with frozen samples. During processing, equipment that contacted the samples, which included the cut-off saw and chisel, was wiped clean of adhering soil particles. A clean sheet of aluminum foil was used as a base during quartering of the frozen sample disks. New out-of-box glassware and high-purity solvents were used for analytical procedures to minimize risk of analytical interference.

Sample Documentation

Upon recovery at the surface, each core segment was inspected, and notes were recorded in a field log book including location, depth, sample time, recovery, and geology. The cores were capped and labeled for location, depth, and orientation (e.g., top and bottom). Packaged cores were placed in coolers with dry ice for shipment. Before shipment, the cooler was sealed with packaging tape. The cooler was sent and received by project team members (Trihydro and/or CSU), so formal chain-of-custody documentation was not required.

Select subsamples were outsourced to an external laboratory for analysis. These subsamples were hand-delivered to a local laboratory (ALS, Fort Collins, Colorado) and included Trihydro chain-of-custody documentation.

APPENDIX G MICROBIOLOGICAL CHARACTERIZATION REPORT

This report presents a summary of methods and results for microbiological analyses conducted as part of this project. Although microbiological characterization was not one of the core analyses conducted in this project, analysis was conducted to supplement geochemical data. Microbiological community preservation presents a potential key advantage to collecting cores cryogenically. At this stage in development, the techniques for microbial extraction and analyses are considered to be works in progress.

Microbiological characterization was conducted using one of the sample quarters generated during processing. Immediately after cutting the core into a frozen disk and quartering, one of the sample quarters was wrapped in aluminum foil and returned to the freezer (-80°C) until DNA extraction. Microbial analysis was performed in triplicate following procedures similar to those described by Irianni-Renno et al. (2016). The samples were pretreated as described by Whitby and Lund (2009), with modifications, to remove potential contaminants (e.g., LNAPL), as described in Irianni-Renno et al. (2016). DNA was quantified via optical density at 260 nm with a Nanodrop™ 2000 reader (Thermoscientific, Wilmington, DE). DNA was extracted in triplicate from each sample and was subsequently stored at -20°C prior to quantitative polymerase chain reaction (qPCR) and next-generation sequencing analysis.

qPCR assays. SYBR™ Green (Life Technologies, Grand Island, NY) qPCR assays were used to quantify the bacterial and archaeal 16S rRNA genes. Genomic DNA extracted *from Desulfovibrio desulfuricans* (ATCC #:27774D-5) and *Methanosarcina acetivorans* (ATCC #: 35395D-5) was used to generate calibration curves for the bacterial and archaeal assays, respectively. The primer sets 27F / 388r and 931AF /1100Ar were used for amplification of bacterial and archaeal 16SrRNA genes, respectively. All assays were performed using an ABI 7300 real-time PCR system (Applied Biosystems, Foster City, CA). Each 25-µl SYBR™Green qPCR reaction included 1X Power SYBR™Green (Life technologies, Grand Island, NY), forward and reverse primers (2.5 µM), magnesium acetate (10 µM), PCR-grade water and 1 ng of DNA template. Thermocycling conditions were as follows: 95˚C for 10 min, followed by 40 cycles of 95˚C for 45 s, 56˚C for 30 s, and 60˚C for 30 s. Dissociation curve analysis was conducted to confirm amplicon specificity.

Next generation sequencing analysis. Sequencing analysis was performed by Research and Testing Laboratories, LLC (Lubbock, TX) using an Illumina MiSeq System (Illumina, San Diego, CA). Community profiling was performed targeting bacterial 16S rRNA genes with primers 28F and 519r and archaeal 16S rRNA genes with primers 517f and 909r.

Data analysis. Results from the microbial communities characterized were evaluated at multiple taxonomic levels. In this report, data are presented at three taxonomic levels (phylum, order and genus) for Bacteria and at two taxonomic levels (phylum and order) for Archaea (Appendix G).

Orders and genera that represent less than 3% of the community are combined with those that are unclassified, and reported as “other.” Phyla that represent less than 0.05% of the community are combined with those that are unclassified and reported as “other.” In addition, when analyzing the bacterial communities at the genus level, organisms that have been shown to share functional capabilities, such as putative sulfate reducers, iron reducers, and methane oxidizers, were reported in the following groups:

- Putative sulfate reducers included organisms belonging to the following genera: *Desulfotomaculum* spp., *Thermodesulfovibrio* spp., *Desulfatirhabdium* spp., *Desulfobacterium* spp, *Desulfobulbus* spp. *Desulfocella* spp., Unclassified *Desulfobacteraceae*, *Desulfovibrio* spp., *Desulfobacca* spp., *Desulfomonile* spp., *Desulfovirga* spp., *Desulfuromonas* spp., *Thermodesulfobacterium* spp.
- Putative iron reducers included organisms belonging to the following genera: *Rhodoferax* spp., *Geobacter* spp., *Geothermobacter* spp.
- Putative methane oxidizers included organisms belonging to the following genera: *Methylocapsa* spp., *Methylocella* spp., *Methylobacterium* spp., *Methylocystis* spp., *Methylosinus* spp., *Methylobacillus* spp., Unknown *Methylophilaceae*.

Results. Results are shown below for each of the six soil-coring locations.

Location SA1

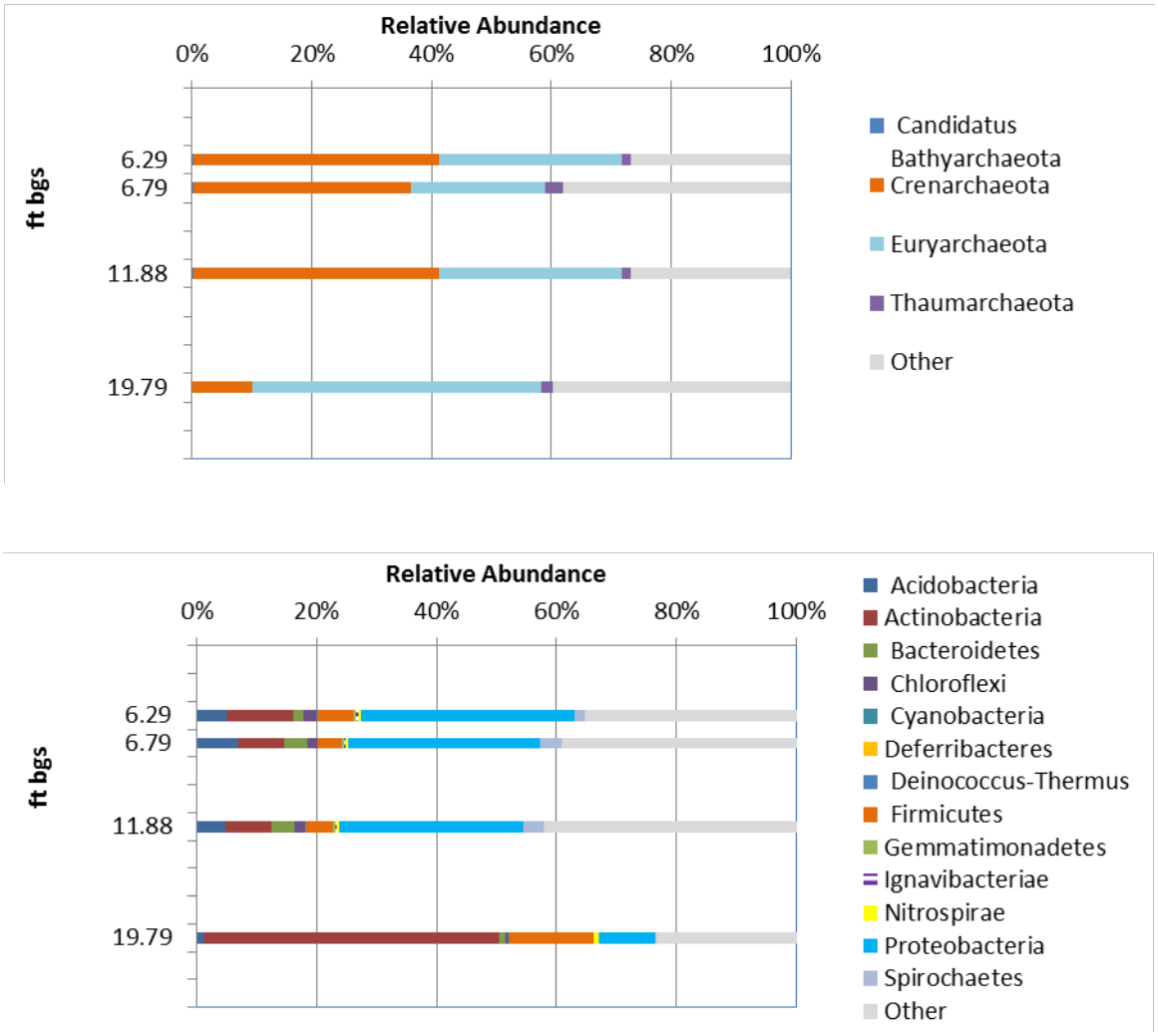


Figure G-1: Archaeal (upper) and Bacterial (lower) Community Composition of Subsamples Collected from Core SA1: PhylumLlevel.

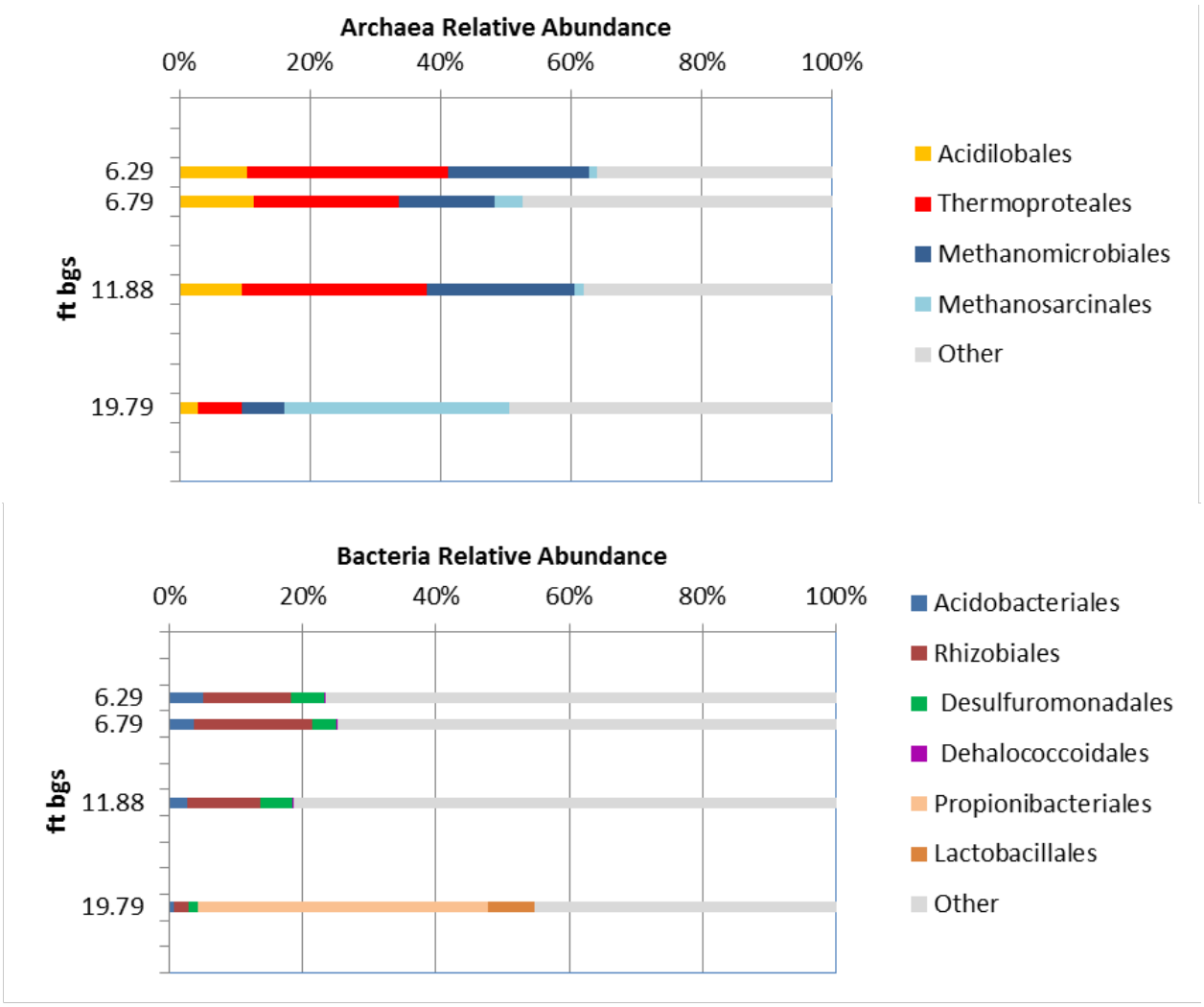


Figure G-2: Archaeal and Bacterial Community Composition of Subsamples Collected from Core SA1: Order Level.

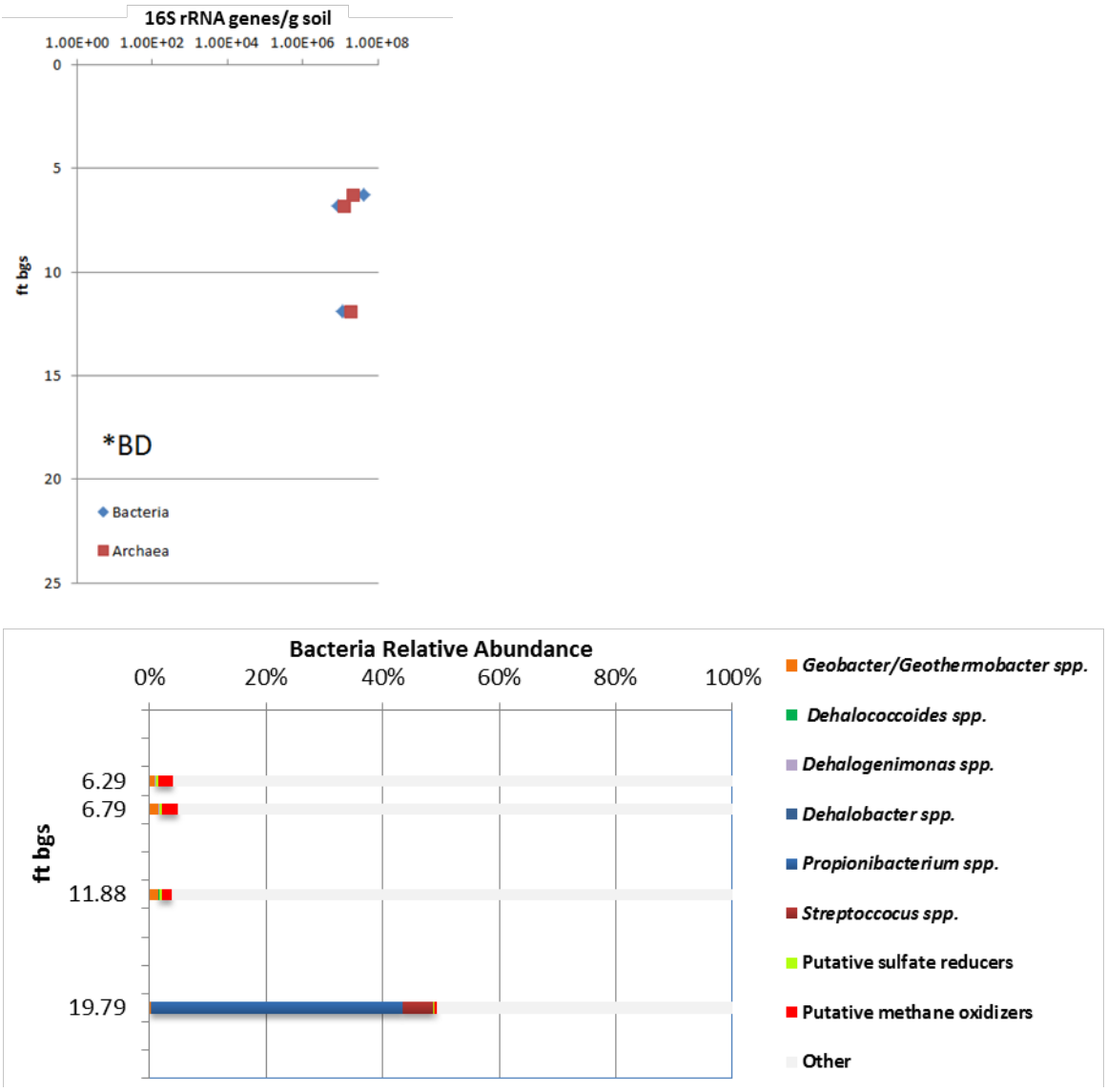


Figure G-3: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core SA1: Genus Level.

No Bacteria or Archaea were detected in qPCR analysis of the sample collected at 19.78 ft bgs.

- The samples collected at 6.29 and 6.79 ft bgs had insignificant numbers of dechlorinators present. Putative methane oxidizers were identified (red) in these samples. Approximately between 16 and 19% of the archaeal community was identified as methanogens (Fig. G-2).
- The sample collected at 11.88 ft bgs contained insignificant numbers of dechlorinators. Methane oxidizers were present. Approximately 1.5% of the bacterial community was identified as putative iron reducers belonging to the genera *Geobacter* or *Thermogeobacter*.
- The sample collected at 19.79 ft bgs yielded very low amounts of DNA. Both bacterial and archaeal 16S rRNA genes were below detection limit when quantified via qPCR. Sample sequencing was only successful for bacterial genes.

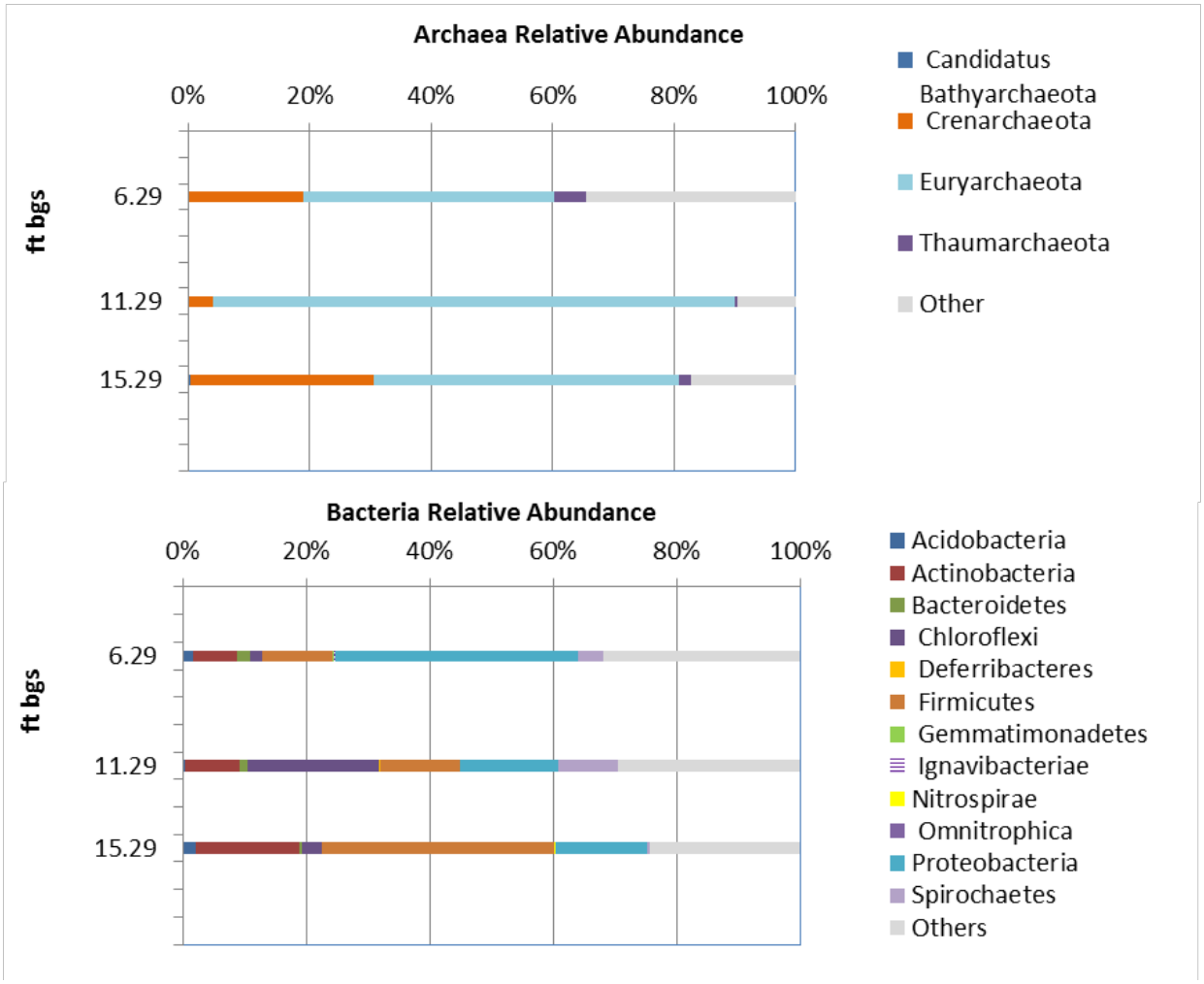


Figure G-4: Archaeal and Bacterial Community Composition of Subsamples Collected from Core SA2: Phylum Level.

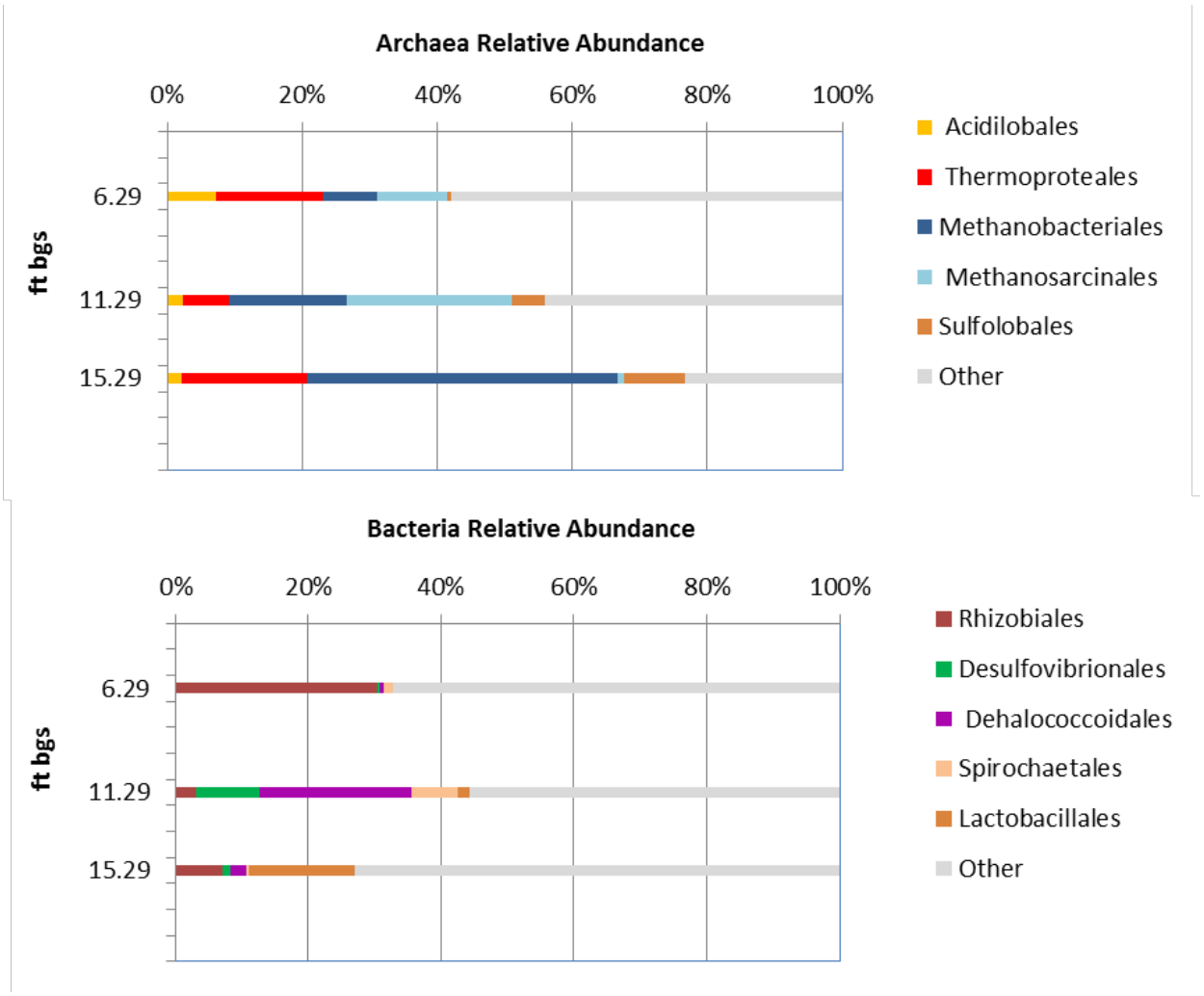


Figure G-5: Archaeal and Bacterial Community Composition of Subsamples Collected from Core SA2: Order Level.

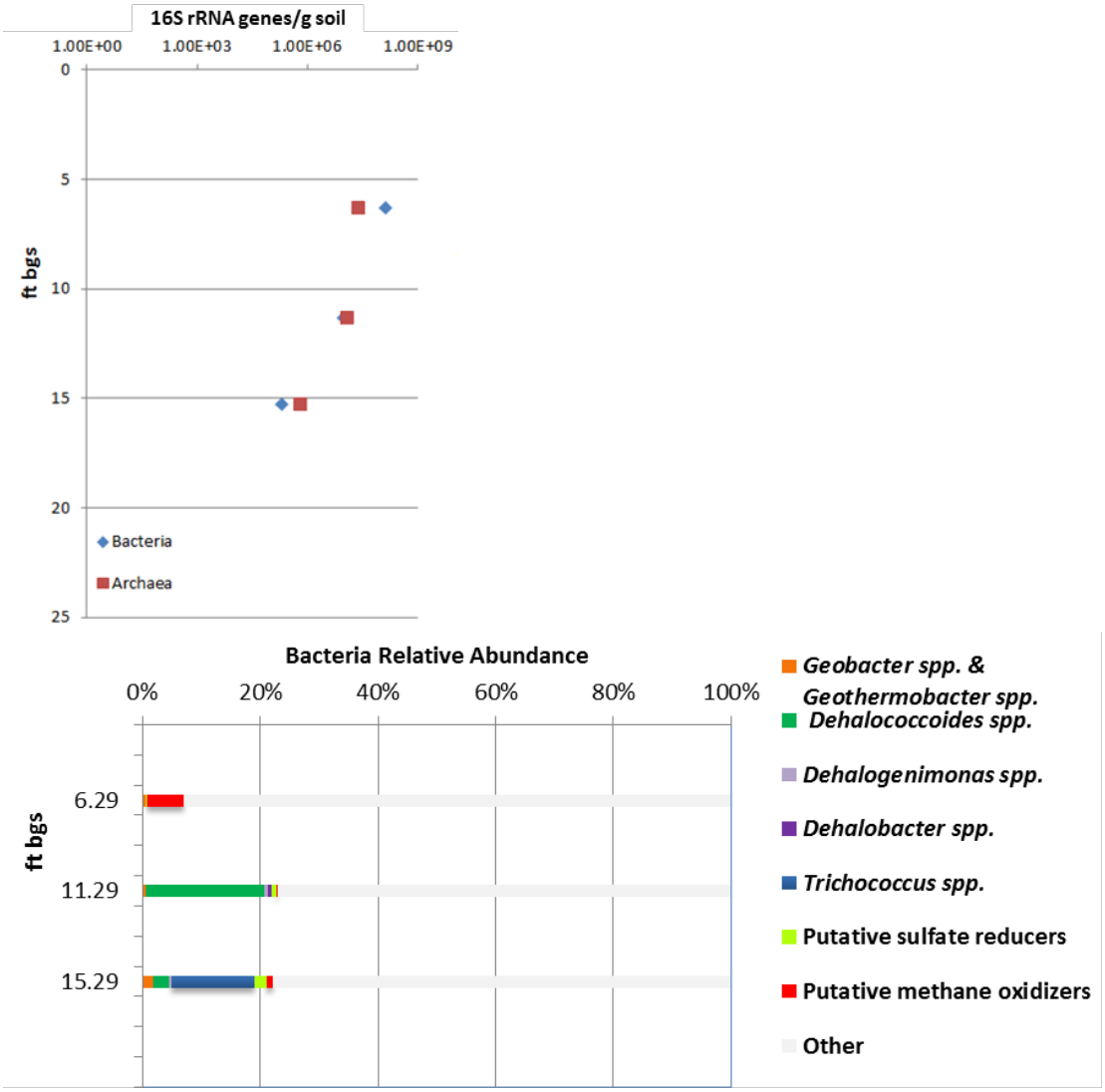
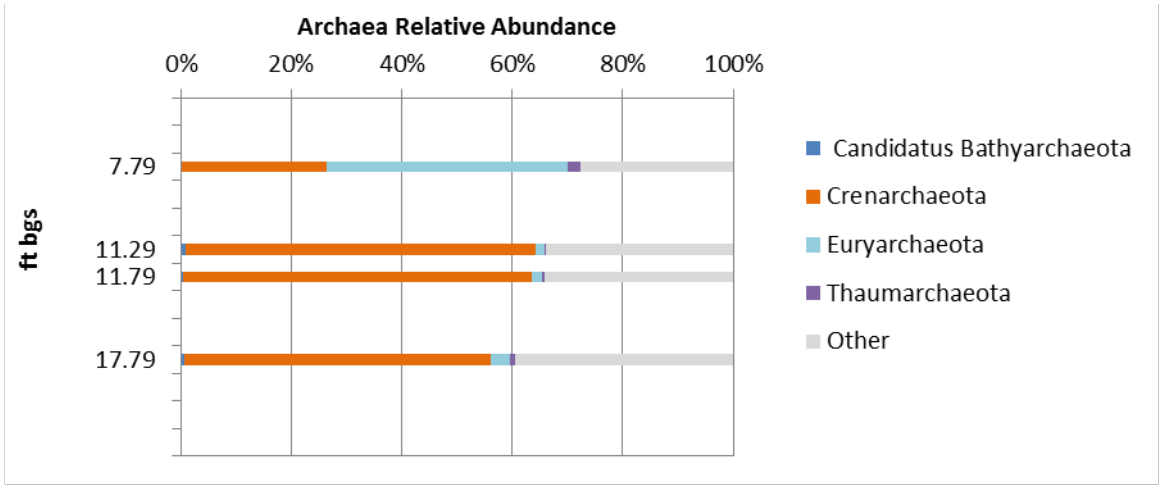


Figure G-6: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core SA2: Genus Level.

- Insignificant amounts of dechlorinators and putative iron reducers were found in the sample collected at 6.29 ft bgs. This sample had relatively high organic content (almost 3% by weight). Approximately 40% of the archaeal community of this sample corresponds to putative methanogens (Fig. G-5).
- The sample collected at 11.29 ft bgs contained significant numbers of putative dechlorinators belonging to the genus *Dehalococcoides* (20.1%); this finding is consistent with high levels of cis-DCE and ethylene measured in the sample. Approximately 73.2% of the archaeal community was identified as methanogenic, which is consistent with the higher methane concentrations measured in this sample.
- The sample collected at 15.29 ft bgs contained some dechlorinators (2.7%). Part of the bacterial community (14%) was identified as members of the genus *Trichococcus.* 1.5% of the sequenced bacterial community belonged to either the genera *Thermogeobacter* or *Geobacter*.



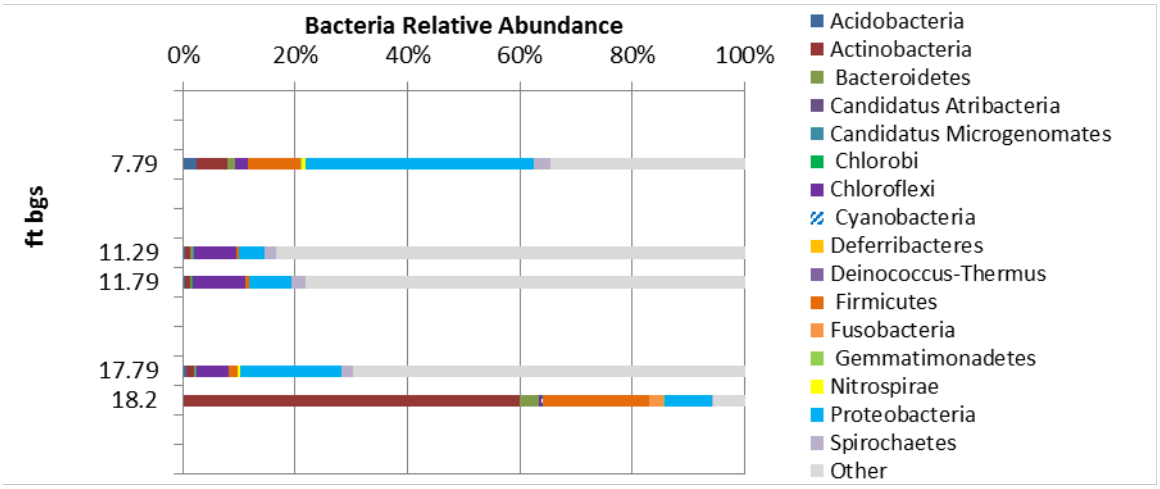


Figure G-7: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1A: Phylum Level.

The sample collected at 18.2 ft bgs yielded no archaeal results.

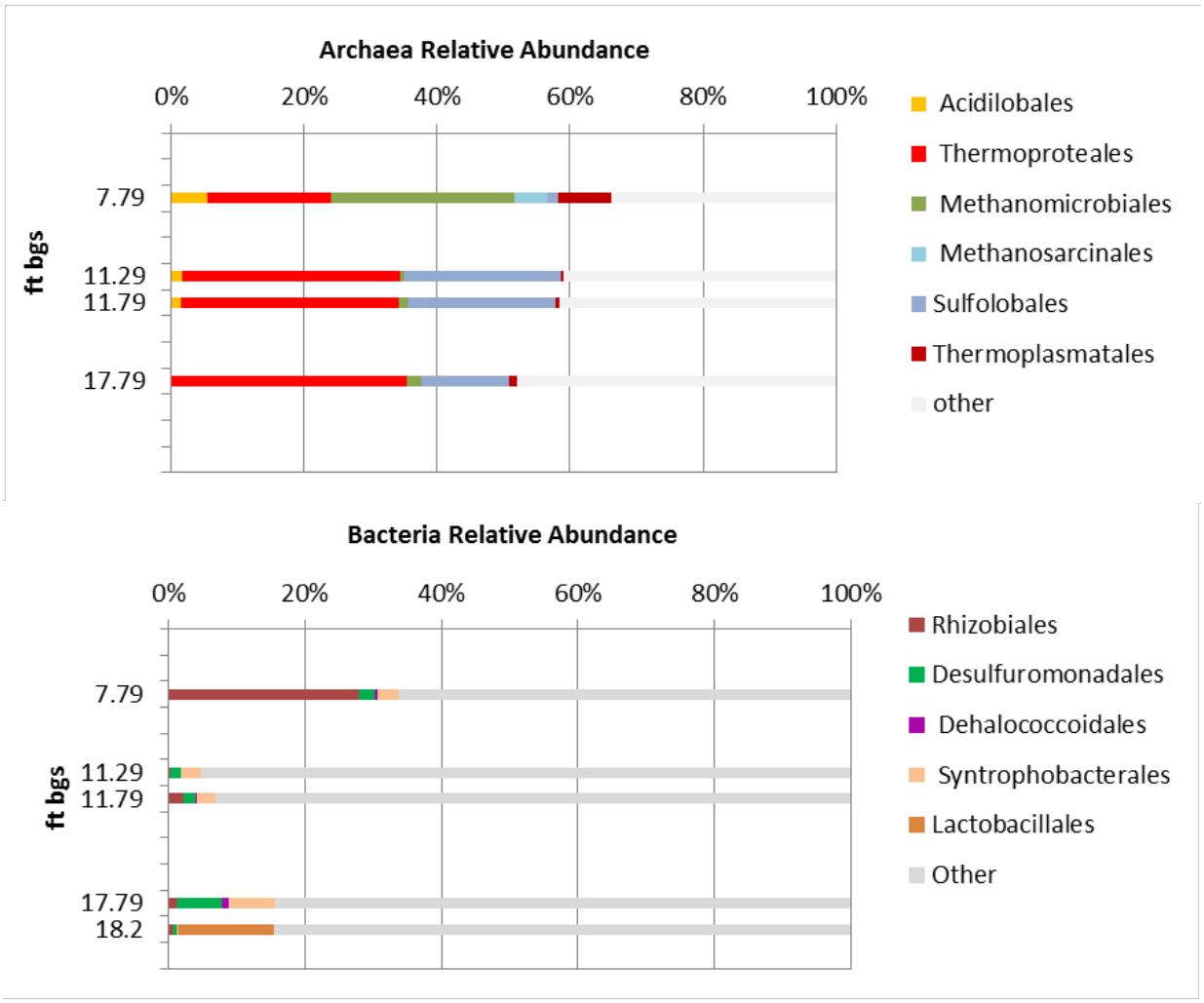


Figure G-8: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1A: Order Level.

The sample collected at 18.2 ft bgs yielded no archaeal results.

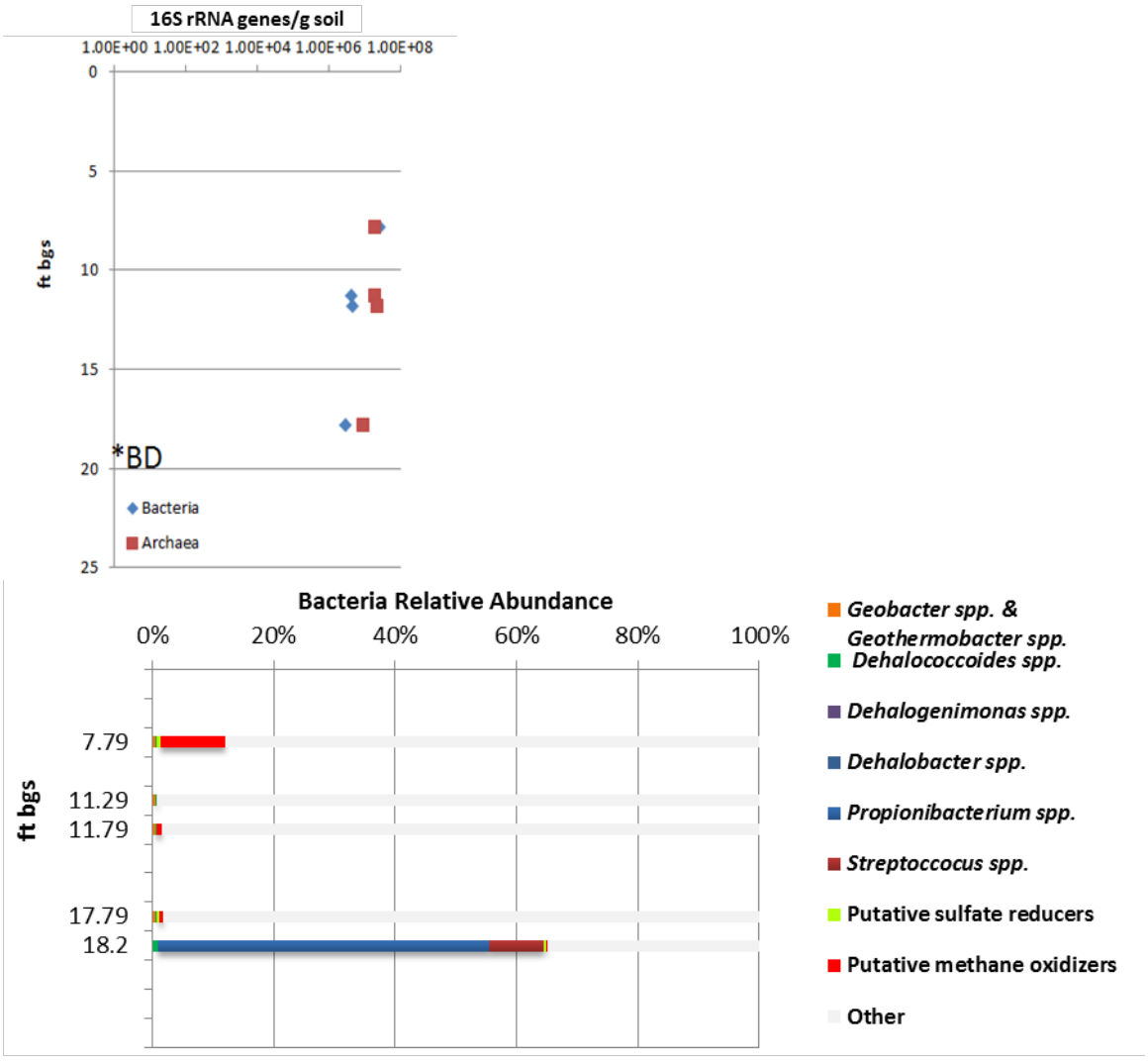


Figure G-9: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG1A: Genus Level.

No Bacteria or Archaea were detected in qPCR analysis of the sample collected at 18.2 ft bgs.

- The sample collected at 7.79 ft bgs contained some putative methane oxidizers. Approximately 32% of the archaeal community was identified as methanogens (Fig. G-8).

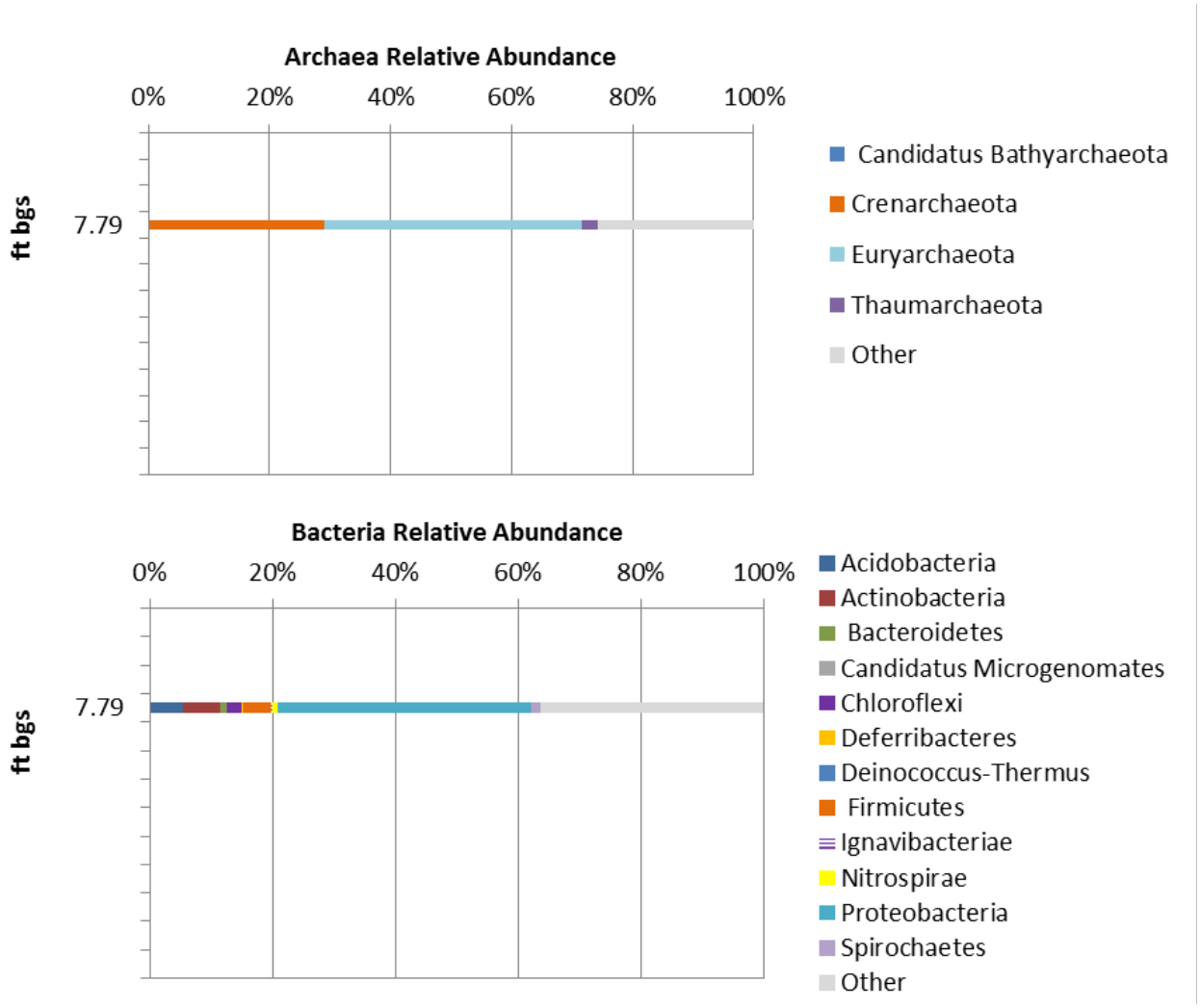


Figure G-10: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1B: Phylum Level.

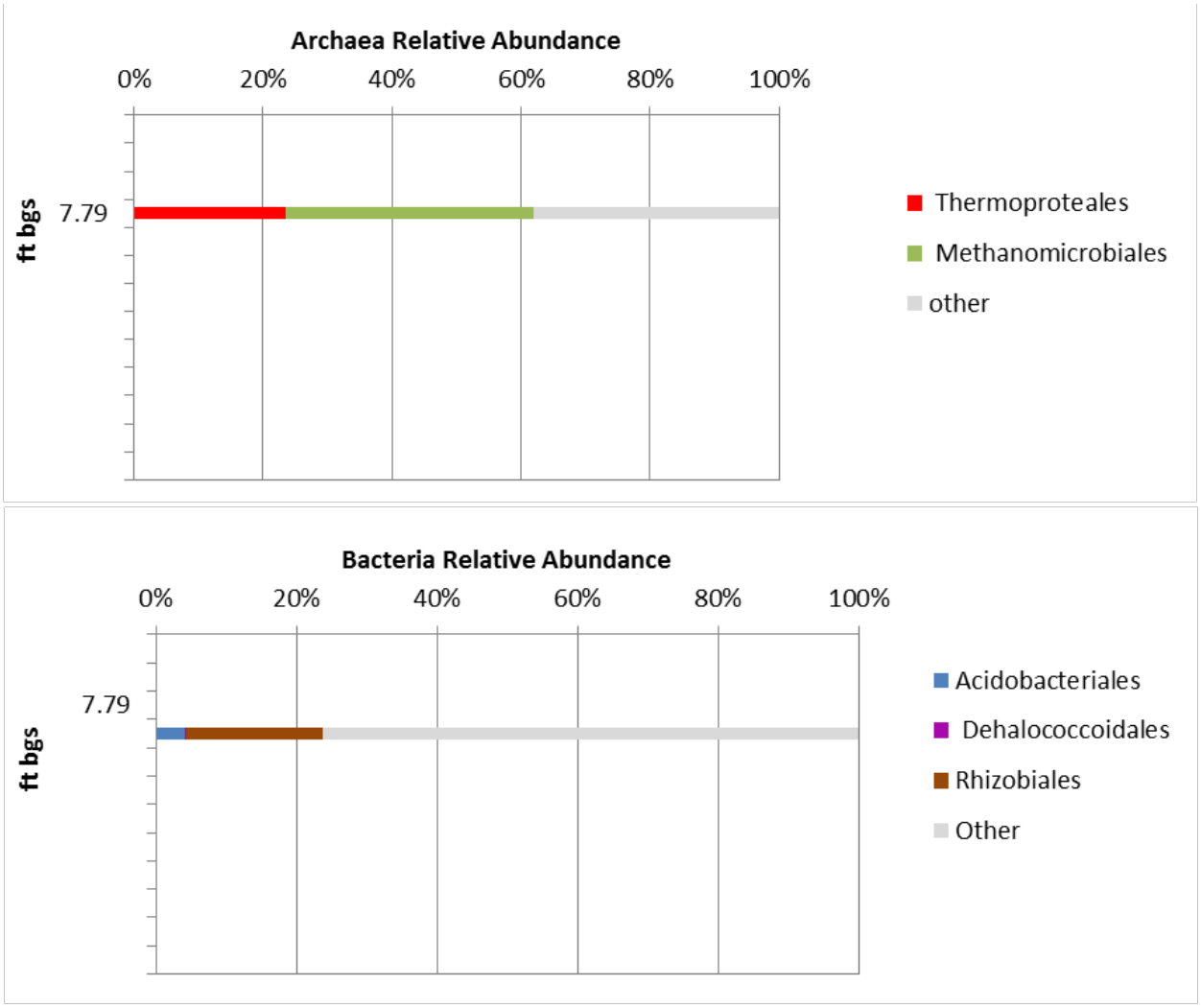


Figure G-11: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG1B: Order Level.

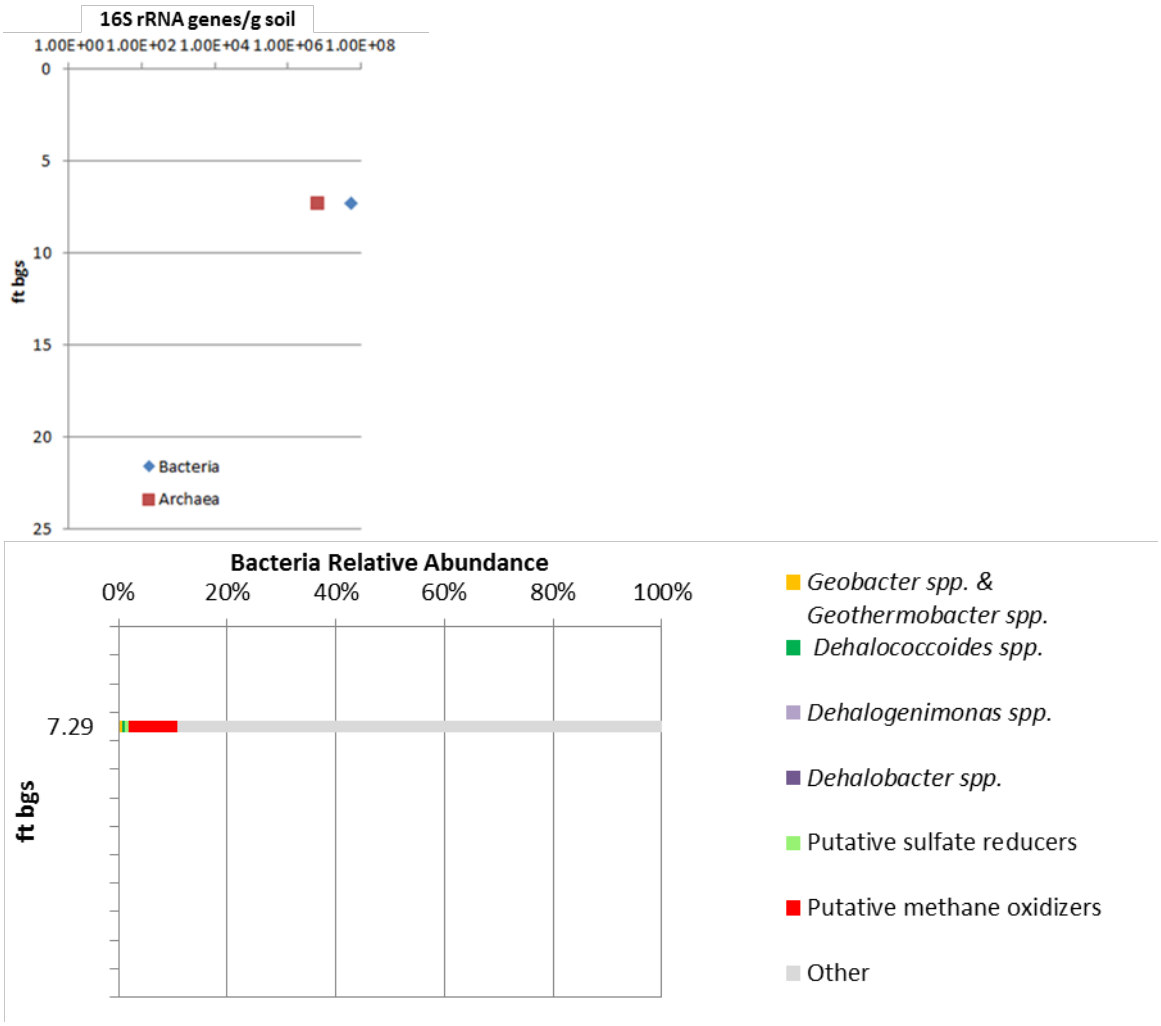


Figure G-12: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG1B: Genus Level.

- No significant numbers of dechlorinators were found in this sample. Methane oxidizers were present. Approximately 31% of the archaeal community was identified as methanogens (Fig. G11).

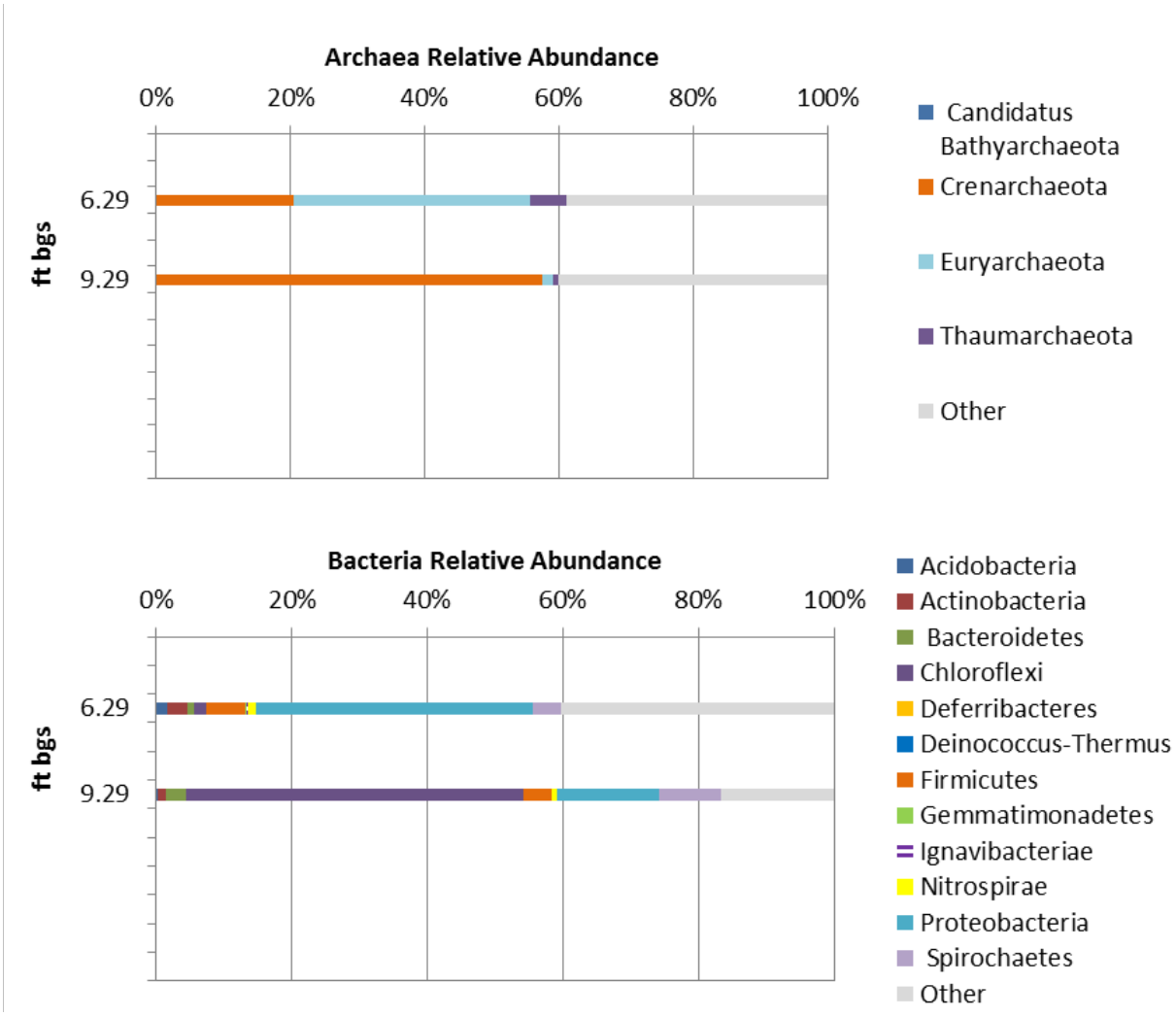


Figure G-13: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2A: Phylum Level.

Figure G-14: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2A: Order Level.

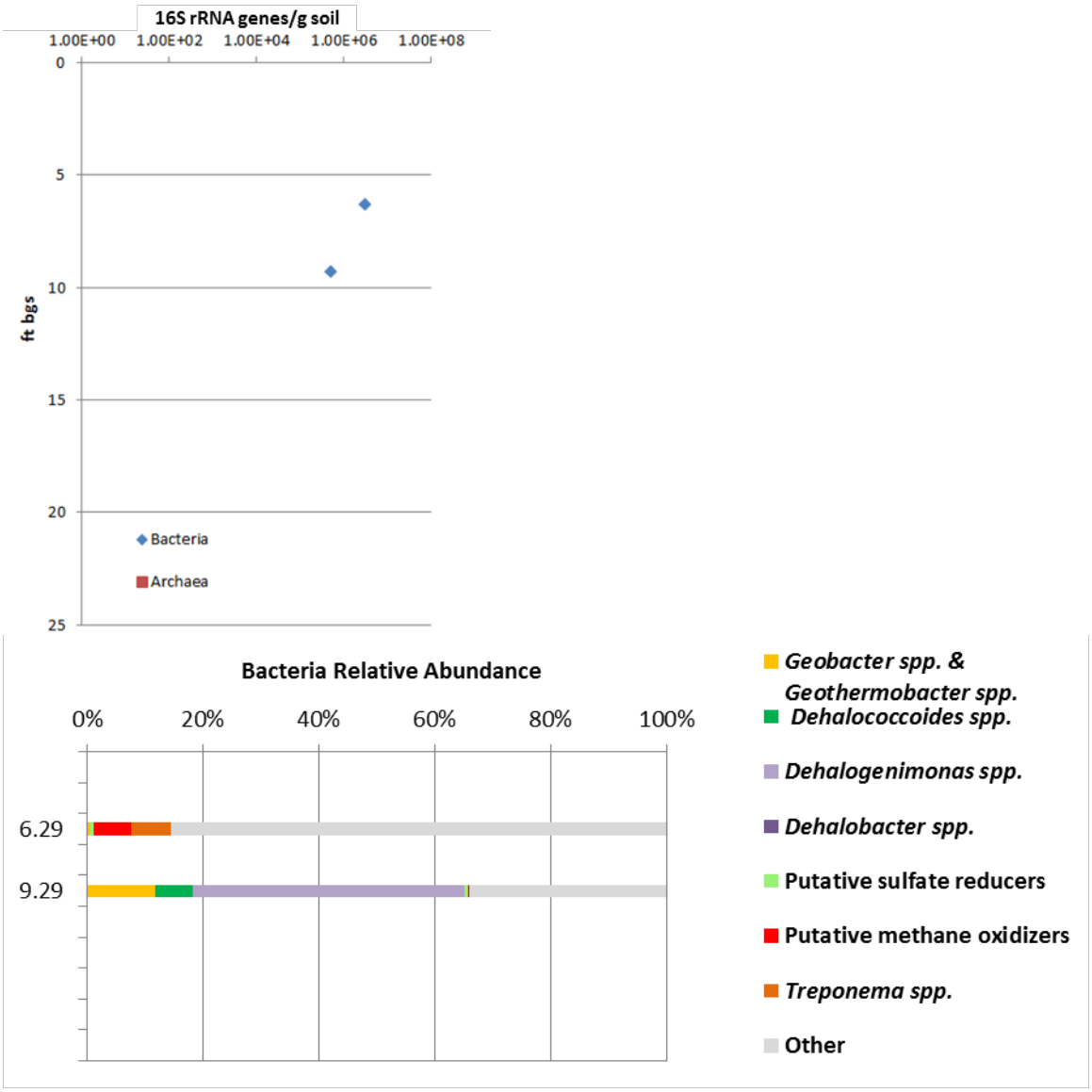


Figure G-15: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG2A: Genus Level.

No Archaea were detected in qPCR analysis of either sample analyzed from core DG2A.

No Archaea were detected through qPCR. For the sample collected at 9.29 ft bgs, 43% of the characterized bacterial community belonged to the genus *Dehalogenimonas*. Some members of this genus have been identified as able to grow by organohalide respiration, coupling the oxidation of H_2 to the reductive dehalogenation of polychlorinated alkanes. Additionally, 6% of the characterized bacteria within this sample belonged to the genus *Dehalococcoides*. Ethylene and *c*DCE were present in this sample. A substantial part of the bacterial community was identified as putative iron reducers. 11 % of the characterized bacterial community belongs to either the genus *Geobacter* or to the genus *Thermogeobacter*. Relative to other analyzed samples, large amounts of ferrous iron were detected within this sample.

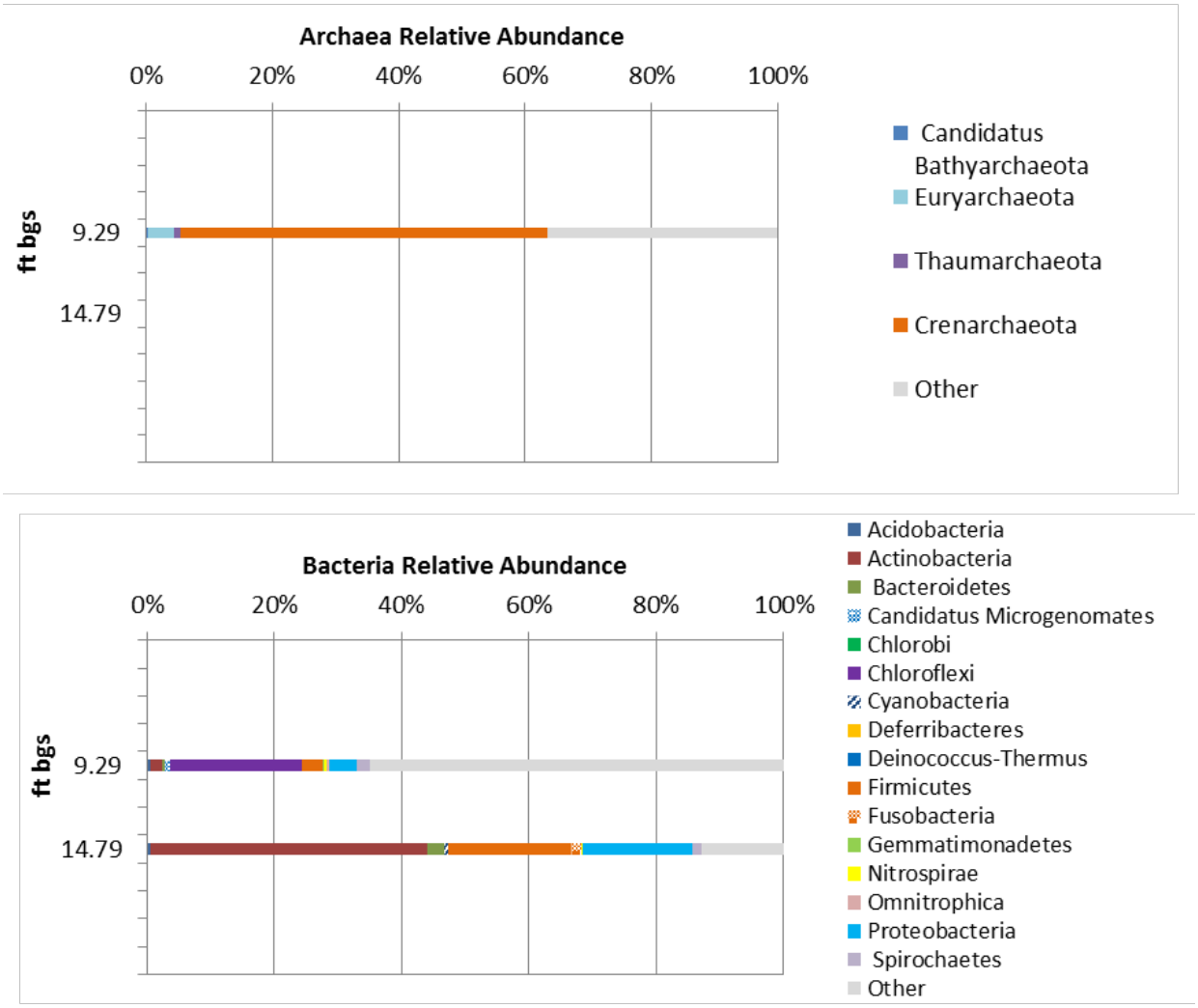


Figure G-16: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2B: Phylum Level.

No Archaea were detected at 14.79 ft bgs, via sequencing analysis of the archaeal 16S rRNA gene.

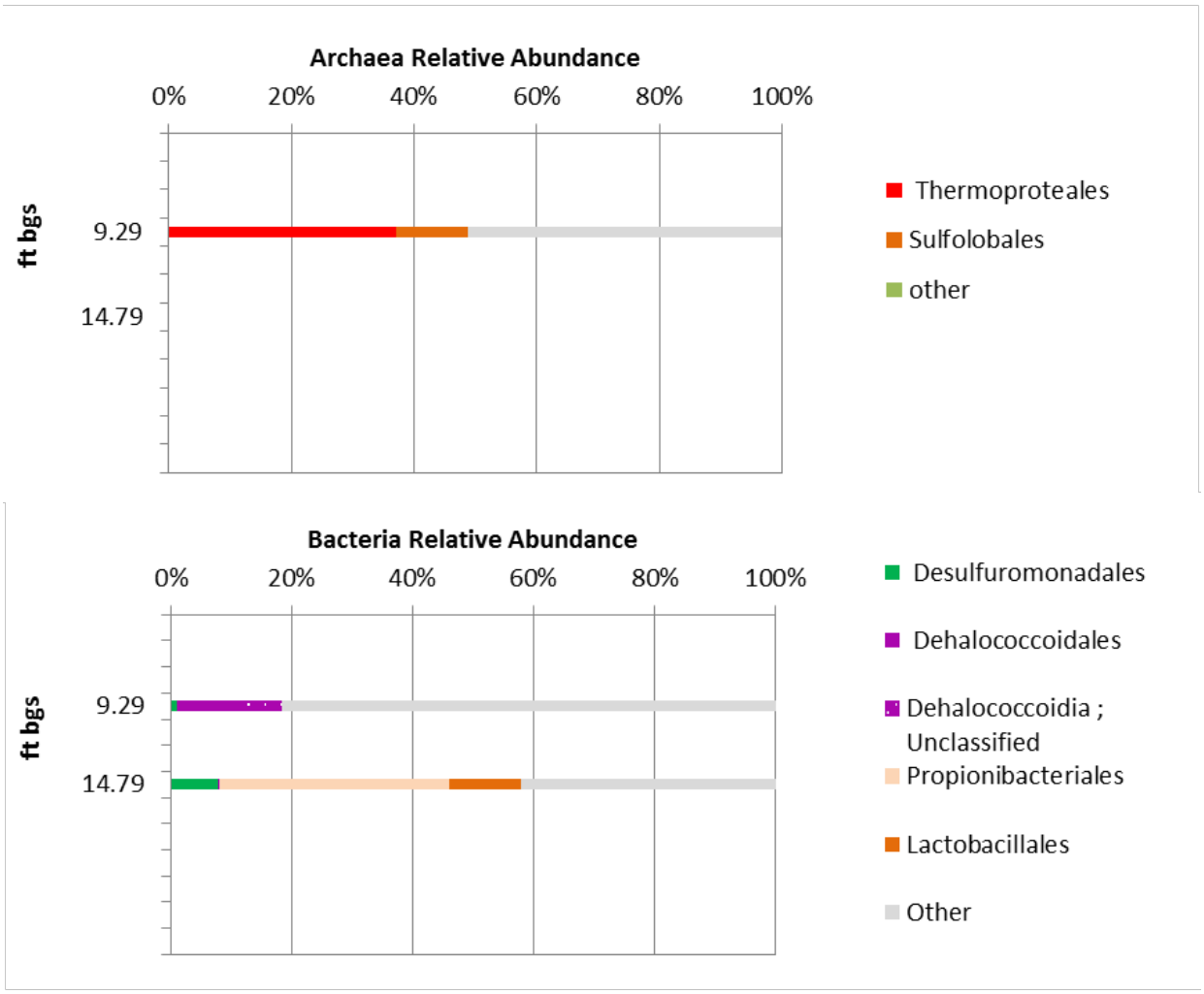


Figure G-17: Archaeal and Bacterial Community Composition of Subsamples Collected from Core DG2B: Order Level.

No Archaea were detected at 14.79 ft bgs, via sequencing analysis of the archaeal 16S rRNA gene.

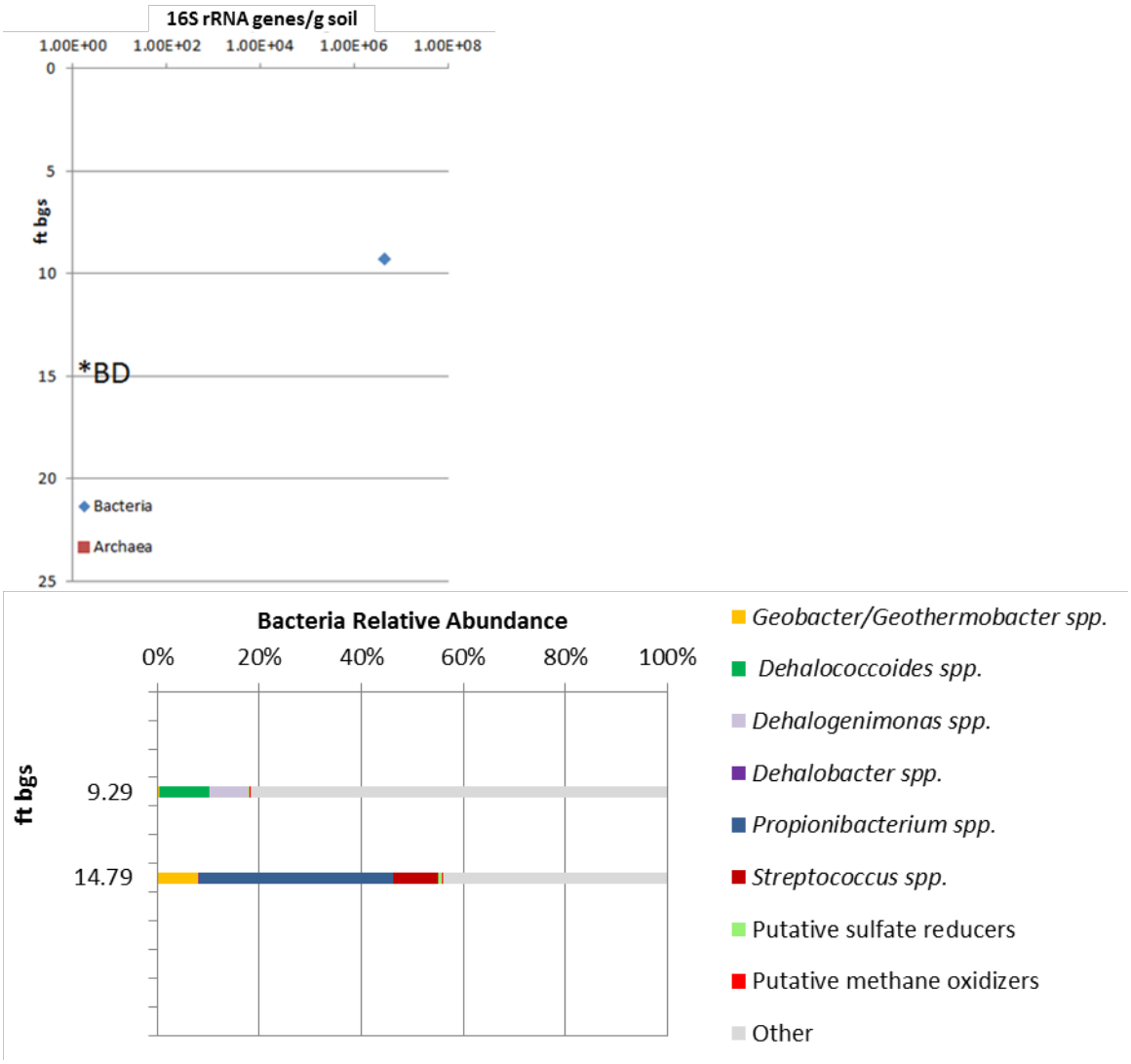


Figure G-18: Results of the qPCR Analyses and Bacterial Community Composition of Subsamples Collected from Core DG2B: Genus Level.

No Archaea were detected in qPCR analysis of either sample analyzed from core DG2B and no Bacteria were detected in qPCR analysis of the sample collected at 14.79 bgs.

No Archaea were detected through qPCR in either of the samples presented above. Sequencing of the archaeal 16S rRNA genes yielded no results. Approximately 9.9% of the characterized bacterial community analyzed for the sample collected at 9.29 ft bgs belonged to the genus *Dehalogenimonas*. 7.5% of the characterized bacteria within this sample belonged to the genus *Dehalococcoides*. Ethylene and *c*DCE were present in this sample as well.

Subsamples collected at 13.79, 14.29, 15.79 and 18.79 ft bgs were also analyzed from this core, but little or no DNA was recovered. Therefore, no downstream sample analysis was possible.

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APPENDIX H TABULATED C_3 DATA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
75	SA1	3.29	0	0.29	0.12	0	ND	15	ND	ND	0	NA	ND	NA	NA	NA	NA	3	NA
74	SA1	3.79	ND	0.13	ND	ND	ND	6.7	ND	ND	0	1.9	3.8	240	15	350	NA	3	NA
73	SA1	4.29	0.1	0.15	0.08	ND	ND	3.4	ND	ND	ND	NA	NA	NA	NA	NA	NA	2.4	NA
79	SA1	6.29	0	0.29	ND	ND	ND	21	ND	ND	0	1.9	3.9	220	10	760	NA	2.9	NA
78	SA1	6.79	ND	0.2	0.17	ND	ND	7.8	ND	ND	0	1.9	10	150	6.6	92	0.9	3	ND
80	SA1	11.88	ND	0.17	ND	ND	ND	14	ND	ND	0	1.9	2.1	170	11	540	NA	3.2	NA
82	SA1	14.21	ND	ND	ND	ND	ND	3.8	ND	ND	0	NA	NA	NA	NA	NA	NA	3.2	NA
81	SA1	14.29	ND	ND	ND	ND	ND	5.4	ND	ND	0	1.9	2.6	170	12	120	NA	3	NA
83	SA1	16.79	ND	ND	ND	ND	ND	8.7	ND	ND	0.1	6.5	18	220	13	37	0.2	3	NA
85	SA1	18.79	ND	ND	ND	ND	ND	5.7	ND	ND	0.1	4.7	15	200	13	69	NA	3	NA
84	SA1	19.29	ND	0.02	ND	ND	ND	1.6	ND	ND	0	4.7	3.6	180	27	150	NA	3.2	NA
91	SA1	19.71	ND	0.11	ND	ND	ND	0.2	ND	ND	0	1.9	ND	110	7.4	540	0.4	3	NA
90	SA1	19.79	ND	0.12	ND	ND	ND	0.7	ND	ND	0	1.9	ND	120	9.2	570	NA	3	NA
89	SA1	20.29	ND	0.23	0.06	ND	ND	1	ND	ND	0	1.9	ND	130	9.5	470	NA	3	NA
88	SA1	20.79	ND	0.45	0.27	ND	ND	0.5	ND	ND	0	1.9	ND	200	8.9	720	NA	2.9	NA
87	SA1	21.29	ND	0.53	0.15	ND	ND	0.3	ND	ND	0	1.9	ND	230	6.9	480	NA	3	ND
86	SA1	21.79	ND	0.48	0.21	ND	ND	0.2	ND	ND	ND	1.9	ND	290	10	470	0.4	2.9	NA
94	SA2	3.29	ND	0.07	0.85	0	ND	4.4	ND	ND	0	1.9	ND	790	13	470	NA	2.9	NA
93	SA2	3.79	ND	0.14	0.35	ND	ND	13	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	NA
92	SA2	4.29	ND	0.07	ND	0	ND	8.6	ND	ND	0.1	30	31	900	9.8	33	NA	3	NA
96	SA2	6.29	ND	ND	0.15	ND	ND	4.2	ND	ND	0	NA	NA	NA	NA	NA	NA	3	NA
95	SA2	6.79	ND	0.17	0.29	ND	0.1	6.1	ND	ND	0.1	1.9	ND	34	ND	11	2.8	3.1	NA
98	SA2	9.04	ND	0.08	0.2	ND	ND	8.6	ND	0	0.2	1.9	ND	1100	4.7	400	NA	3	NA
97	SA2	9.29	ND	0.05	ND	ND	ND	9.2	ND	ND	0.4	NA	NA	NA	NA	NA	NA	3.1	NA
101	SA2	11.21	ND	0.03	ND	ND	ND	2.5	ND	0.4	0.2	NA	NA	NA	NA	NA	NA	3.1	NA
100	SA2	11.29	ND	0.05	ND	ND	ND	5.6	ND	0.9	0.4	48	ND	3300	12	40	NA	3	NA
99	SA2	11.79	ND	ND	ND	ND	ND	8.1	ND	1.4	0.7	3	2.6	2100	3.5	150	0.3	3.2	NA
103	SA2	13.79	ND	0.04	ND	ND	ND	5.4	ND	0.4	0.5	1.9	ND	2100	13	57	NA	3.2	NA
102	SA2	14.21	ND	0.03	ND	ND	ND	1.7	ND	0.1	0.2	NA	NA	NA	NA	NA	NA	2.9	NA
107	SA2	15.29	ND	0.04	ND	ND	ND	0.4	ND	ND	0	1.9	ND	1800	15	48	NA	3	NA
106	SA2	15.79	ND	0.05	ND	ND	ND	0.7	ND	ND	0.1	NA	NA	NA	NA	NA	0.3	3	NA
105	SA2	16.29	ND	0.05	ND	ND	ND	0.8	ND	ND	0	NA	NA	NA	NA	NA	NA	3.1	NA
104	SA2	16.79	ND	0.03	ND	ND	ND	1.2	ND	ND	0.1	1.9	ND	1700	0.8	11	NA	3.1	NA
109	SA2	18.79	ND	0.03	ND	ND	ND	1	ND	ND	0.1	1.9	4.5	1300	2	83	0.2	3	NA
108	SA2	19.29	ND	0.02	ND	ND	ND	0.7	ND	ND	0.1	2.7	5.5	1200	10	37	NA	3.1	NA
171	DG1A	7.29	ND	0.09	ND	ND	ND	1.6	ND	ND	0.2	NA	NA	NA	NA	NA	NA	2.6	NA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
170	DG1A	7.79	ND	0.02	ND	ND	ND	6	ND	ND	0.6	1.9	ND	480	17	2600	NA	2.6	NA
169	DG1A	8.29	ND	0.01	ND	ND	0.2	0.3	ND	0.6	1.7	NA	NA	NA	NA	NA	NA	2.8	NA
168	DG1A	8.79	ND	0.14	0.13	ND	1.4	1.3	ND	1.1	0.8	62	34	680	6.7	1100	0.4	3	NA
167	DG1A	9.29	ND	0.3	1.8	ND	7.5	1.5	ND	4.4	0.9	2.1	1.9	780	0.4	3400	NA	2.8	NA
175	DG1A	10.71	ND	0.01	ND	ND	ND	7.7	ND	5.9	8	NA	NA	NA	NA	NA	NA	2.7	NA
174	DG1A	10.79	ND	ND	ND	ND	ND	2.8	ND	2.4	3.3	19	8.5	910	10	1300	6	2.7	NA
173	DG1A	11.29	ND	ND	ND	ND	ND	11	ND	5.1	11	1.9	1.5	1300	12	1700	NA	2.4	ND
172	DG1A	11.79	ND	0.01	ND	ND	ND	11	ND	2.2	11	NA	NA	NA	NA	NA	NA	2.7	NA
181	DG1A	12.21	ND	ND	ND	ND	0.2	2.1	ND	0.1	2.7	NA	NA	NA	NA	NA	NA	2.7	NA
180	DG1A	12.29	ND	ND	ND	ND	0.3	2.1	ND	0.1	2.4	13	12	860	11	1600	NA	2.9	NA
179	DG1A	12.79	ND	ND	ND	ND	0.3	2.8	ND	0.1	2.8	3.9	1.8	800	14	3200	NA	2.9	NA
178	DG1A	13.29	ND	ND	ND	ND	ND	1.9	ND	ND	1.2	NA	NA	NA	NA	NA	NA	3.2	NA
177	DG1A	13.79	ND	ND	ND	ND	ND	1.5	ND	ND	0.9	7.5	37	430	7.7	69	NA	3.2	NA
176	DG1A	14.29	ND	0	ND	ND	ND	1.1	ND	ND	0.5	NA	NA	NA	NA	NA	NA	3.1	NA
186	DG1A	14.79	ND	ND	ND	ND	ND	0.8	ND	ND	0.3	11	54	630	9.7	32	NA	3	NA
185	DG1A	15.29	ND	ND	ND	ND	ND	0.5	ND	ND	0.2	2.7	42	570	11	60	0.3	3.1	NA
184	DG1A	15.79	ND	0.01	ND	ND	ND	0.4	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	ND
183	DG1A	16.29	ND	0	ND	ND	ND	0.2	ND	ND	0.1	2.2	22	530	9.5	320	NA	3.1	NA
182	DG1A	16.79	ND	ND	ND	ND	ND	0.4	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	NA
191	DG1A	17.29	ND	ND	ND	ND	ND	0.3	ND	ND	0	17	28	700	16	660	0.6	3.1	NA
190	DG1A	17.79	ND	ND	ND	ND	ND	0.1	ND	ND	0	NA	NA	NA	NA	NA	NA	2.9	NA
189	DG1A	18.29	ND	ND	ND	ND	ND	0.1	ND	ND	0	1.9	20	570	6.7	230	NA	3.1	ND
188	DG1A	18.79	ND	ND	ND	ND	ND	0.1	ND	ND	0	NA	NA	NA	NA	NA	NA	3.1	NA
187	DG1A	19.29	ND	ND	ND	ND	ND	0.1	ND	ND	0	1.9	81	17	ND	19	NA	3.2	NA
196	DG1B	7.29	ND	ND	ND	ND	0.1	7.8	ND	0.1	0.3	1.9	ND	410	13	1800	NA	2.6	NA
195	DG1B	7.79	ND	ND	ND	ND	ND	4.1	ND	0	0.1	NA	NA	NA	NA	NA	NA	2.5	NA
194	DG1B	8.29	ND	ND	ND	ND	ND	17	ND	ND	1.2	1.9	ND	340	17	1700	1.9	2.9	NA
193	DG1B	8.54	ND	ND	ND	ND	ND	7.1	ND	ND	1.2	NA	NA	NA	NA	NA	NA	2.6	NA
192	DG1B	9.29	ND	0.04	ND	ND	ND	2.9	ND	1	2.1	1.9	ND	440	11	660	NA	3	NA
200	DG1B	10.29	ND	ND	0.12	ND	0.8	5.5	ND	3.4	4.2	1.9	ND	870	17	3200	NA	2.5	NA
199	DG1B	10.79	ND	ND	0.25	ND	1.4	4.4	ND	3.1	3.7	NA	NA	NA	NA	NA	NA	2.4	NA
198	DG1B	11.29	ND	ND	ND	ND	0.7	12	ND	6.5	7.8	2	2.2	33	ND	53	NA	2.4	ND
197	DG1B	11.79	ND	ND	ND	ND	1.2	5.3	ND	4	4.1	1.9	ND	740	0.9	2900	NA	2.5	NA
205	DG1B	12.71	ND	ND	ND	ND	ND	6.9	ND	0.3	1	NA	NA	NA	NA	NA	NA	2.6	NA
204	DG1B	12.79	ND	ND	ND	ND	ND	11	ND	0.3	1.4	1.9	ND	1000	12	5400	3.3	2.5	NA
203	DG1B	13.29	ND	ND	ND	ND	ND	9.2	ND	0	0.9	1.9	ND	650	11	2900	NA	2.8	NA
202	DG1B	13.79	ND	ND	ND	ND	ND	10	ND	ND	1	NA	NA	NA	NA	NA	NA	2.4	NA
201	DG1B	14.29	ND	ND	ND	ND	ND	16	ND	ND	1.2	1.9	ND	27	ND	110	NA	2.7	NA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
210	DG1B	14.79	ND	ND	ND	ND	ND	4.4	ND	ND	0.4	25	9.6	20	ND	98	NA	2.9	NA
209	DG1B	15.29	ND	ND	ND	ND	ND	2.5	ND	ND	0.2	NA	NA	NA	NA	NA	NA	2.8	NA
208	DG1B	15.79	ND	ND	ND	ND	ND	1	ND	ND	0	14	52	14	ND	15	0.2	3.2	NA
207	DG1B	16.29	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA	3.2	NA
206	DG1B	16.79	ND	ND	ND	ND	ND	0.9	ND	ND	0	2.5	9.6	17	ND	9	NA	3.1	NA
215	DG1B	17.29	ND	ND	ND	ND	ND	0.3	ND	ND	0	NA	NA	NA	NA	NA	NA	3.2	NA
214	DG1B	17.79	ND	ND	ND	ND	ND	0.3	ND	ND	ND	24	NA	1.4	ND	ND	0.1	3.2	NA
213	DG1B	18.29	ND	ND	ND	ND	ND	0.2	ND	ND	0	NA	NA	NA	NA	NA	NA	3	NA
212	DG1B	18.79	ND	ND	ND	ND	ND	0.1	ND	ND	ND	4.7	31	15	ND	10	NA	2.9	NA
211	DG1B	19.29	ND	ND	ND	ND	ND	0.1	ND	ND	ND	NA	NA	NA	NA	NA	NA	3.2	NA
137	DG2A	3.29	ND	0.02	0.05	ND	ND	1.5	ND	ND	0	NA	NA	NA	NA	NA	NA	3.2	NA
136	DG2A	3.79	ND	0.03	0.85	0	0.5	0.9	ND	ND	0	1.5	11	130	8.4	14	0.6	3.3	NA
135	DG2A	4.29	ND	0.1	ND	ND	ND	0.6	ND	ND	0	1.9	10	220	0.7	98	NA	3	NA
139	DG2A	6.29	ND	ND	ND	ND	ND	0.6	ND	ND	0	1.9	4.4	240	6.9	230	NA	3	NA
138	DG2A	6.79	ND	ND	ND	ND	ND	1.1	ND	ND	0.1	NA	NA	NA	NA	NA	NA	3	NA
143	DG2A	8.21	ND	1.5	1.9	0	0.5	0.6	ND	0	0	NA	NA	NA	NA	NA	NA	2.8	NA
142	DG2A	8.29	ND	21	22	0.2	7.5	0.5	ND	0	0	1.9	ND	250	13	2100	NA	2.9	NA
141	DG2A	8.79	ND	300	77	0.4	5.3	0.5	ND	0.2	0.1	160	56	880	19	4300	NA	2.7	NA
140	DG2A	9.29	ND	670	43	0.2	2.1	0.8	0	0.2	0.1	560	180	1600	13	6700	26	2.3	NA
148	DG2A	9.79	ND	130	0.59	ND	ND	0.1	0	0	0	8.6	ND	600	15	810	NA	3.2	NA
147	DG2A	10.29	ND	76	0.71	ND	ND	0.1	ND	ND	ND	NA	NA	NA	NA	NA	NA	3.1	NA
146	DG2A	10.79	ND	190	0.98	ND	ND	0.1	ND	ND	0	1.9	1.5	560	13	260	NA	2.7	NA
145	DG2A	11.29	0	290	3.5	0	0.2	0.1	0	0	0	NA	NA	NA	NA	NA	NA	2.7	NA
144	DG2A	11.79	ND	7300	170	ND	ND	0.2	ND	ND	ND	45	9.3	980	18	5000	NA	2.7	NA
152	DG2A	12.79	ND	160	1.7	ND	ND	0.1	0	0	0	NA	NA	NA	NA	NA	NA	3.1	NA
151	DG2A	13.29	0.1	260	1.2	0	ND	0	ND	ND	0	2.5	24	550	7.7	180	NA	3.1	NA
150	DG2A	13.79	ND	90	1.1	0	ND	0.1	0	0	0	NA	NA	NA	NA	NA	NA	3.1	NA
149	DG2A	14.29	ND	120	0.89	0	0.1	0.1	0	0	0	13	24	720	17	240	NA	3.1	NA
161	DG2A	14.79	ND	97	1.3	ND	ND	0.2	0	0	0.2	3	12	840	16	400	0.2	2.9	NA
160	DG2A	15.29	ND	82	1.4	0	0.1	0.2	0	0	0.2	NA	NA	NA	NA	NA	NA	3	NA
159	DG2A	15.79	ND	66	1.4	ND	ND	0.2	0	0.1	0.3	1.5	5.8	710	8.9	440	NA	3	NA
158	DG2A	15.88	ND	120	2.4	ND	ND	0.1	0	0	0.2	NA	NA	NA	NA	NA	NA	3	NA
157	DG2A	15.96	ND	97	2	0	ND	0.1	0	ND	0.2	NA	NA	NA	NA	NA	NA	3	NA
156	DG2A	16.04	ND	93	1.8	ND	ND	0.2	0	0.1	0.4	NA	NA	NA	NA	NA	NA	3.1	NA
155	DG2A	16.13	ND	160	2.6	ND	ND	0.1	0	0	0.2	NA	NA	NA	NA	NA	NA	3.1	NA
154	DG2A	16.29	ND	100	1.9	ND	ND	0.2	0	0.1	0.3	1.9	6.7	650	8.3	410	NA	3	NA
153	DG2A	16.79	ND	61	1.9	ND	ND	0.1	0	0	0.2	NA	NA	NA	NA	NA	NA	3	NA
166	DG2A	17.29	ND	120	2.4	ND	ND	0.2	0	0	0.2	1.9	1.5	32	ND	43	NA	2.8	NA

Sample ID	Location	Depth (ft bgs)	PCE mg/kg	TCE mg/kg	cDCE mg/kg	tDCE mg/kg	VC mg/kg	Methane mg/kg	Acetylene mg/kg	Ethylene mg/kg	Ethane mg/kg	Fe (II) mg/L	Fe-total mg/L	Cl mg/L	NO3 mg/L	SO4 mg/L	foc (%)	Bulk Density	log K
165	DG2A	17.79	ND	130	2.3	ND	ND	0.2	0	0.1	0.3	NA	NA	NA	NA	NA	NA	2.9	NA
164	DG2A	18.29	ND	120	2.4	ND	ND	0.1	0	0	0.1	2.5	3	720	10	390	NA	3	NA
163	DG2A	18.79	ND	140	1.2	ND	ND	0.1	0	ND	0.1	NA	NA	NA	NA	NA	NA	2.9	NA
162	DG2A	19.29	ND	180	0.73	ND	ND	0.1	0	0	0	1.9	ND	750	8.6	530	0.2	2.8	NA
111	DG2B	3.71	ND	0.03	ND	ND	ND	2	ND	ND	0	NA	NA	NA	NA	NA	NA	3	NA
110	DG2B	4.29	ND	0.02	ND	ND	ND	4.1	ND	ND	0	2.4	ND	52	1	1200	NA	3.2	NA
115	DG2B	5.71	ND	0	ND	ND	ND	2.9	ND	ND	0	1.9	21	130	2.6	170	NA	2.9	NA
114	DG2B	5.79	ND	ND	ND	ND	ND	3.3	ND	ND	0.1	NA	NA	NA	NA	NA	NA	2.8	NA
113	DG2B	6.29	ND	ND	0.02	ND	ND	3.6	ND	0	0.9	NA	NA	NA	NA	NA	NA	2.8	NA
112	DG2B	6.79	ND	ND	1.9	ND	1.7	2.9	ND	0.6	0.6	7.3	3.7	88	0.6	2900	1.1	2.8	NA
117	DG2B	8.79	0	0.01	0.8	0	0.9	2.6	ND	0.4	0.4	40	17	110	9.8	1700	1.2	2.8	NA
116	DG2B	9.29	ND	ND	5.2	ND	11	4.4	ND	1.6	0.8	110	38	170	11	3300	NA	2.6	NA
120	DG2B	10.79	ND	ND	0.87	1.5	2	3.8	ND	3.1	1	69	17	9.4	ND	87	NA	3	NA
119	DG2B	11.29	ND	ND	1.7	ND	3.1	1.6	ND	1.7	0.5	NA	NA	NA	NA	NA	NA	3.1	NA
118	DG2B	11.79	ND	ND	5.2	ND	1.4	2.8	ND	3.1	0.6	2.1	14	290	9.6	26	NA	3	NA
124	DG2B	13.21	ND	1.1	8.7	0	5.6	0.5	ND	0.7	0.2	NA	NA	NA	NA	NA	NA	3	NA
123	DG2B	13.29	ND	0.61	5.7	ND	4.2	1.1	ND	1	0.2	1.9	3.3	330	11	170	1.7	3.1	NA
122	DG2B	13.79	ND	3.8	7.9	ND	4.7	0.9	ND	1	0.2	NA	NA	NA	NA	NA	NA	3.1	NA
121	DG2B	14.29	ND	11	6.1	ND	2.9	1.3	ND	1.7	0.2	4.3	37	390	8.2	37	NA	3.1	NA
129	DG2B	14.79	ND	35	8.3	ND	2.8	0.5	ND	0.4	0	2.7	11	550	20	320	NA	3.1	NA
128	DG2B	15.29	ND	45	6.5	0	1.3	0.4	ND	0.5	0	NA	NA	NA	NA	NA	NA	3.1	NA
127	DG2B	15.79	ND	75	7.9	ND	1.5	0.4	ND	0.5	0	1.2	8.1	460	11	170	NA	3.1	NA
126	DG2B	16.29	ND	31	3.9	ND	0.3	0.3	ND	0.3	0	NA	NA	NA	NA	NA	NA	3.2	NA
125	DG2B	16.79	ND	31	3.4	ND	ND	0.1	ND	0.1	0	1.9	5.3	480	11	320	NA	3.1	NA
134	DG2B	17.29	ND	42	2.8	ND	0.6	0.2	ND	0.1	0	NA	NA	NA	NA	NA	NA	3.2	NA
133	DG2B	17.79	ND	28	1.8	ND	0.1	0.1	ND	0	ND	2.8	13	17	ND	26	0.2	3.2	NA
132	DG2B	18.29	ND	28	2	ND	0.2	0.1	ND	0	ND	NA	NA	NA	NA	NA	NA	3.2	NA
131	DG2B	18.79	ND	32	1.8	ND	0.1	0.1	ND	0	ND	7.3	84	470	10	160	NA	3.1	NA
130	DG2B	19.29	ND	27	1.4	ND	ND	0.1	ND	0	ND	NA	NA	NA	NA	NA	NA	3	NA